MONTREAL PROTOCOL
ON SUBSTANCES THAT DEPLETE THE OZONE LAYER

UNEP

1994 Report of the Solvents, Coatings and Adhesives Technical Options Committee

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MONTREAL PROTOCOL ON SUBSTANCES THAT DEPLETE THE OZONE LAYER

pursuant to
Article 6
of the Montreal Protocol;
Decision IV/13 (1993)
by the Parties to the Montreal Protocol

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GLOSSARY

Acute toxicity	The short-term toxicity of a product in a single dose. Can be divided into oral, cutaneous, and respiratory toxicities.
Adsorption	Not to be confused with absorption. Adsorption is a surface phenomenon of some substances that can form a physicochemical bond with specific materials.
Aerosol Spray	A means of atomizing liquids by propelling them from a pressurized container through a suitable valve by either a liquified or pressurized gas.
Alcohols	A series of hydrocarbon derivatives with at least one hydrogen atom replaced by an -OH group. The simplest alcohols (methanol, ethanol, n-propanol, and isopropanol) are good solvents for some organic soils, notably rosin, but are flammable and can form explosive mixtures with air. The use of flammable solvents requires caution and well-designed equipment.
Aqueous cleaning	Cleaning with water to which suitable detergents, saponifiers, or other additives may be added.
Azeotrope	A mixture of chemicals is an azeotrope if the vapour composition is identical to that of the liquid phase. This means that the distillate of an azeotrope is theoretically identical to the solvents from which it is distilled. In practice, the presence of contaminants in the solvent may upset the azeotropy.
Biodegradable	Products are classified as biodegradable if they can be easily broken down or digested by living organisms.
BOD	An abbreviation for biochemical oxygen demand, a measure of the biodegradability of wastewater.
Carbon tetrachloride	A chlorocarbon solvent with an ODP of approximately 1.1. It is also considered toxic and a probable human carcinogen (classified as a B2 carcinogen by US EPA). Its use is strictly regulated in most countries and it is used primarily as a feedstock material for the production of other chemicals.
CFC	An abbreviation for chlorofluorocarbon.
CFC-112	1,1,2,2-tetrachloro-1,2-difluoroethane.
CFC-113	1,1,2-trichloro-1,2,2-trifluoroethane.

CFC-113a	An isomer of CFC-113; 1,1,1-trichloro-2,2,2-trifluoroethane.
Chelation	Chelation is the solubilisation of a metal salt by forming a chemical complex or sequestering. One way of doing this is with ethylenediaminetetraacetic acid (EDTA) salts which have a multidentate spiral ligand form that can surround metallic and other ions.
Chlorocarbon	An organic substance composed of chlorine and carbon, e.g., carbon tetrachloride.
Chlorofluorocarbon	An organic substance composed of chlorine, fluorine, and carbon atoms, usually characterised by high stability contributing to a high ODP.
Chronic toxicity	The long-term toxicity of a product in small, repeated doses. Chronic toxicity can often take many years to determine.
COD	An abbreviation for chemical oxygen demand.
Conformal coating	A protective material applied in a thin, uniform layer to surfaces of an electronic assembly.
Controlled atmosphere soldering	A soldering process done in a relatively oxygen-free atmosphere. The process greatly reduces oxidation of the solder, so that less flux is required, thereby reducing or eliminating the need for cleaning.
Defluxing	The removal of flux residues after a soldering operation. Defluxing is a part of most high-reliability electronics production.
Detergent	A product designed to render soils (e.g., oils and greases) soluble in water, usually made from synthetic surfactants.
Dichloromethane	A chlorocarbon solvent used extensively for metal cleaning. Also known as methylene chloride.
Dry cleaning	A common term for cleaning garments in organic solvents, as opposed to water.
Dry film	A photoresist or photoimageable solder mask applied to printed circuits by lamination.
Fatty acids	The principal part of many vegetable and animal oils and greases. Also known as carboxylic acids, which embrace a wider definition. These are common contaminants which use solvents for their removal. They are also used to activate fluxes.

Flux	A chemical employed in the soldering process to facilitate the production of a solder joint. It is usually a liquid or solid material, frequently based on rosin (colophony).
Greenhouse effect	A thermodynamic effect whereby energy absorbed at the earth's surface and normally radiated back out to space in the form of long-wave infrared radiation, is retained due to gases in the atmosphere, causing a rise in global temperature. CFCs that cause ozone depletion are "greenhouse gases," with a single CFC-113 molecule having the same estimated global warming effect as 14,000 carbon dioxide molecules.
Halocarbon	Any organic substance where at least one hydrogen atom in the hydrocarbon molecule has been replaced by a halogen atom (fluorine, chlorine, bromine, iodine, or astatine).
Halons	Substances used as fire-extinguishing agents and having high ODPs.
HCFC	An abbreviation for hydrochlorofluorocarbon.
HCS	An abbreviation for hydrocarbon/surfactant (intra).
HFC	An abbreviation for hydrofluorocarbon.
Hybrid circuits	Electronic circuits, with or without integral passive components, which are formed by the application of conductive and resistive patterns to a vitrous or ceramic substrate.
Hydrocarbon	An organic substance composed only of hydrogen and carbon. Gaseous or volatilized hydrocarbons are flammable.
Hydrocarbon derivative	A hydrocarbon whose molecule has been modified by adding atoms other than hydrogen and carbon, e.g., alcohols.
Hydrocarbon/surfactant solvents	A mixture of low-volatility hydrocarbon solvents with surfactants, allowing the use of a two-phase cleaning process. The first phase is solvent cleaning in the blend and the second phase is water washing and rinsing to remove the residues of the blend and any other water-soluble soils. The surfactant ensures the water-solubility of the otherwise insoluble hydrocarbon. Sometimes called semi-aqueous solvents.
Hydrochlorocarbon	An organic substance composed of hydrogen, chlorine, and carbon, e.g., trichloroethylene.

Hydrochlorofluorocarbon	An organic substance composed of hydrogen, chlorine, fluorine, and carbon atoms. These chemicals are less stable than CFCs, thereby having generally lower ODPs, usually abbreviated as HCFC.
IARC	An abbreviation for International Agency for Research on Cancer.
Infra-red soldering	A method of reflow soldering where the solder and the parts being joined are heated by the incidence of infra-red radiation in air, in an inert gas, or in a reactive atmosphere.
Isopropanol	See alcohols.
Leadless surface mount component	A surface mount component (SMC) whose exterior consists of metallized terminations that are an integral part of the component body.
Lifetime	The folded-e lifetime is the time required for the quantity of a substance in the atmosphere to be reduced to 1/e (0.368) of its original quantity. The folded-e lifetime of CFC-113, for example, is about 80 years.
Low-solids flux	A flux which contains little solid matter, thereby reducing or eliminating the need for cleaning. See no-clean flux.
MEA	An abbreviation for monoethanolamine.
Metal cleaning	General cleaning or degreasing of metallic surfaces or assemblies generally with unspecified cleanliness requirements.
Methyl chloroform	See 1,1,1-trichloroethane.
Monoethanolamine	A saponifier capable of reacting with rosin fluxes and fatty acids. The reaction products are essentially water-soluble. Usually abbreviated as MEA.
No-clean flux	A flux whose residues do not have to be removed from an electronics assembly; therefore, no cleaning is necessary. This type of flux is often characterized by low quantities of residues.
ODP	An abbreviation for ozone depletion potential.
Organic acid (OA) flux	See water-soluble flux.
Ozone	A gas formed when oxygen is ionised. Ozone partially filters certain wavelengths of UV light from the earth. Ozone is a desirable gas in the stratosphere, but it is toxic to living organisms at ground level (see volatile organic compound).

Ozone depletion	Accelerated chemical destruction of the stratospheric ozone layer. Chlorine and bromine free radicals liberated from relatively stable chlorinated, fluorinated, and brominated products by ultraviolet radiation in the ozone layer are the most depleting species.
Ozone depletion potential	A relative index of the ability of a substance to cause ozone depletion. The reference level of 1 is assigned as an index to CFC-11 and CFC-12. If a product has an ozone-depletion potential of 0.5, a given weight of the product in the atmosphere would, in time, deplete half the ozone that the same weight of CFC-11 or CFC-12 would deplete. Ozone-depletion potentials are calculated from mathematical models which take into account factors such as the stability of the product, the rate of diffusion, the quantity of depleting atoms per molecule, and the effect of ultraviolet light and other radiation on the molecules.
Ozone layer	A layer in the stratosphere, at an altitude of approximately 10-50km, where a relatively high concentration of ozone filters harmful ultraviolet radiation from the earth.
PCB	An abbreviation for printed circuit board.
Pentafluoropropanol	A fluorinated alcohol.
Perchloroethylene	A perhalogenated chlorocarbon solvent used extensively in industrial degreasing and dry cleaning.
Perhalogenation	An organic molecule is perhalogenated if all of the parent hydrogen atoms in a hydrocarbon are replaced with halogen atoms (astatine, bromine, chlorine, fluorine, or iodine). For example, carbon tetrachloride (CCl_4) is perchlorinated methane (CH_4). Chloroform ($CHCl_3$) is an example of a simple chlorinated methane, where only three of the hydrogen atoms have been replaced.
Photoresist	A photomechanical product, in the form of a liquid or a laminated dry film, used in the manufacture of printed circuits. Certain types of these products use large quantities of ozone-depleting hydrochlorocarbon solvents, usually 1,1,1-trichloroethane. Dichloromethane is used for stripping some types.
Precision cleaning	Cleaning of high-precision mechanical parts and electronic sensory devices, as opposed to general metal cleaning. This is usually done in "clean-rooms," with low particulate contamination, to specific standards.

POTW	Publicly Owned Treatment Works.
Printed circuit	A printed circuit is a component for interconnecting other components. It usually consists of a metallic conductor pattern on an organic insulating substrate. After fabrication, it is known as a printed circuit board (PCB); after assembly with components it is known as a printed wiring assembly (PWA). [Terminology different in Europe and USA.]
PWA	An abbreviation for printed wiring assembly.
Reflow soldering	A method of electronics soldering commonly used with surface mount technology, whereby typically a paste formed of solder powder and flux suspended in an organic vehicle is melted by the application of heat.
Rosin	A solid resin obtained from pine trees. It is frequently used as a flux, usually with additives.
Rosin flux	A flux whose main constituent is rosin. There are several categories of rosin flux, often designated by the codes R (pure rosin), RMA (rosin, mild activation), RA (rosin, activated usually with free chloride ions), RSA (rosin, super activated).
SA Flux	Synthetic activated fluxes.
Saponifier	A chemical designed to react with organic fatty acids, such as rosin, some oils and greases, etc., to form water-soluble soaps. This is a method for defluxing and degreasing. Saponifiers are usually alkaline and may be mineral based (sodium hydroxide or potassium hydroxide) or organic based (water solutions or monoethanolamine).
Semi-aqueous solvents	Another name for hydrcarbon/surfactant (HCS) solvents. The UNEP Committee recommends hydrocarbon/surfactant (HCS) solvents as the more descriptive and accurate nomenclature.
SMC	An abbreviation for surface mount component.
Solder mask (resist)	A polymeric coating applied to bare printed circuits which leaves only the pads or leads, designed to be subsequently soldered, as bare metal.
Solvent	An aqueous or organic product designed to clean a component or assembly by dissolving and/or displacing the contaminants present on its surface.
Solvent containment	Means of reducing the emission of solvents (e.g., CFCs) into the environment. This technique usually involves improving the design and operation of the equipment in which the solvent is used.

Surface mount component (SMC)	A component capable of being attached to a PCB using surface mount technology. The component may be either leaded or leadless.
Surface mount technology (SMT)	A technique for assembling SMCs on the surface of PCBs and PWAs, as opposed to inserting leads through holes.
Surfactant	A chemical to reduce the surface tension of water. Also referred to as surface-active agents. Detergents are made primarily from surfactants.
Terpene	Any of many homocyclic hydrocarbons with the empirical formula $C_{10}H_{16}$. Turpentine is mainly a mixture of terpenes. See hydrocarbon/surfactant solvents.
1,1,1-trichloroethane	A hydrochlorocarbon solvent with an estimated ODP of 0.1. Also known as methyl chloroform.
Ultrasonic cleaning	Immersion cleaning where mechanical energy formed by cavitational implosions close to the surfaces being cleaned significantly aids the cleaning operation.
Vapour-phase cleaning	A cleaning process, usually with CFC-113 solvent or hydrochlorocarbon solvents, where the final rinse is achieved by condensing solvent vapours on the parts being cleaned.
Vapour-phase (condensation) soldering	A method of reflow soldering where the solder and the parts being joined are heated in the vapour of a perfluorinated substance whose boiling point is usually in the range of 215-260°C. In some types of equipment designed for this process, a less expensive secondary vapour blanket of CFC-113 is used.
Volatile organic compound (VOC)	These are constituents that will evaporate at their temperature of use and which, by a photochemical reaction under favourable climatic conditions, will cause atmospheric oxygen to be converted into potentially smog-promoting tropospheric ozone.*
Water-soluble flux	A flux whose post-soldering residues may be removed by a water wash. Such fluxes are usually very active, so adequate defluxing is an essential part of their use. They are also known as Organic Acid (OA) fluxes or inorganic acid fluxes.
Wave soldering	Also known as flow soldering, a method of mass soldering electronics assemblies by passing them, after fluxing, through a wave of molten solder.

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* Legally, some countries classify all organic substances which evaporate at ambient temperatures as VOCs, irrespective of their ozone-promoting properties.

EXECUTIVE SUMMARY: SOLVENTS, COATINGS, AND ADHESIVES TOC

Developed Country Progress in Eliminating Ozone-Depleting Solvents

Most developed country suppliers and consumers of ozone depleting solvents are halting production and use earlier than mandated or expected. A few enterprises have made unwise first choices of alternatives and substitutes and are changing to better options.

However, significant problems exist in the European Union (EU), where many companies began their investments too late and may not be able to halt their use prior to the 1 January 1995 EU phaseout of production. Furthermore, some large companies in developed countries may have been over-confident that their uses would qualify as essential and consequently may not have allowed enough time for a smooth transition. Varying sizes of enterprises, but especially small- and medium-sized ones, are identified in many developed countries as possibly being unaware, unprepared, and financially unable to make necessary investments in time to avoid chemical shortages and price increases that could jeopardize their businesses.

Procrastination in implementing alternatives and substitutes could lead to significant price increases for stockpiled and recycled ODSs manufactured prior to the phaseout. Dramatic price increases could stimulate illegal markets in imported solvents. In the immediate future, shortages of ozone-depleting substances (ODSs) for solvent applications could cause companies to switch to chlorinated solvents and/or HCFCs, if allowed, because these solvents can often be used in existing equipment.

Military Progress

In January 1994 the North Atlantic Treaty Organization (NATO) held its 2nd international conference on "The Role of the Military in Protecting the Ozone Layer". Participants from Algeria, Belarus, Belgium, Brazil, Canada, Denmark, France, Germany, Hungary, India, Italy, Japan, Kenya, Latvia, Lithuania, Norway, Pakistan, Poland, Portugal, Romania, Russia, Spain, Slovakia, Sweden, Taiwan, Thailand, Netherlands, Turkey, Ukraine, United Kingdom, United States, and Uruguay attended the meeting. NATO members reported that they are meeting or exceeding the production phaseout goals of the Montreal Protocol and EU members reported that they are meeting their more stringent goals. Part of the reason for this progress has been the leadership of policy makers in some ministries of defence who realized that global environmental protection is part of national security and also recognized that they cannot continue to depend on chemicals that will be unavailable or increasingly expensive.

Germany, Norway, and Sweden reported that they have virtually eliminated the use of ozone-depleting solvents in military applications.

German, Swedish, UK, and US participants reported comparable progress in identifying and documenting alternatives and substitutes for civilian aircraft maintenance including options that provide equal or improved cleaning, surface preparation, and bonding. The International Cooperative for Ozone Layer Protection (ICOLP) announced plans to invite U.S. Environmental Protection

Agency (EPA) and the National Aeronautics and Space Administration (NASA) to join their global project to phase out ODSs in aerospace operations. NASA and U.S. EPA are considering the proposal.

The meeting resulted in several recommendations being made to NATO:

- Share information on critical uses (e.g. gaseous and liquid oxygen systems, guidance systems, rocket motors) via electronic databases, publications, workshops and informal working groups.
- Foster and support streamlined universal qualification processes and procedures.
- Revise the existing military documentation.
- Further investigation, certification, and publication of alternatives and substitutes for unresolved applications including critical adhesive bonds in rocket motor manufacturing, cleaning and verification of gaseous and liquid oxygen systems, and other specific precision cleaning such as gyroscope bearings in space systems that must operate for many years without maintenance.
- Speed awareness and introduction of proven technologies by utilizing "tiger teams" of experienced engineers and scientists to help implement these technologies in military applications.

Developing Country Progress:

In some cases, technology cooperation with developing countries has already been highly successful or has prepared countries to take prompt action once incentives and financing are in place. Examples include Mexico, Thailand, Turkey, and Malaysia. An important conclusion from investigations of solvent use in developing countries is that enterprises must be motivated and prepared to accept new technology. This motivation can result from government regulation, a clearly articulated industry phaseout strategy, price increases, product shortages, or supply uncertainty for ozone-depleting substances. Some technology cooperation efforts have been prematurely attempted in countries where enterprises and national governments were not prepared, and as a consequence little actual investment progress has been made.

Some regional and national conferences and workshops have not been as successful as they could have been because the preconditions for change had not been met. The Committee recommends that conference planners more completely involve local industry, industry associations, and chambers of commerce in the planning and that they determine whether the preconditions for change are in place. If it is determined that a conference is useful, conferences should be organized and announced far in advance. It has been the experience of the Committee in developed and developing countries that representatives of small- and medium-sized solvent-using enterprises do not travel long distances for meetings based on general presentations. They are short of funds and their manufacturing engineers are very busy. This makes ensuring the presence of a motivational framework all the more important.

One problem common to all countries, but especially developing countries, is that domestic small- and medium-sized enterprises that use ODSs are difficult to identify, may not welcome government officials, and may not be easy to convince that a change is necessary. It is likely that many of such users will only make changes when the price increases, when shortages develop, when domestic regulations are in place, or when multinational companies require suppliers to phaseout.

Concerns of unannounced changes in speciality products:

The Committee cautions that manufacturers may eliminate ODSs from products without notifying customers. There is the possibility that the manufacturer may not appreciate that their product is used in a particular application where the ODSs provided a necessary performance characteristic that is not duplicated by the reformulated product. Use of such reformulated materials and products under these circumstances could be costly or dangerous to life and health. The solution is for manufacturers of speciality products to better communicate to end-users, changes in product ingredients and to cooperate with end-users on performance testing of the new products.

Some Parties may have interpreted process agent use of controlled substances as subject to phaseout. Other Parties may have interpreted such use as feedstock not subject to the phaseout. In 1994 the Committee was unable to recommend exemptions for process agent use under the Essential Use Criteria.

At the October 6-7, 1994 Meeting of the Parties to the Protocol, it was decided:

> "...for an interim period of 1996 only, (Parties may) treat chemical process agents in a manner similar to feedstock, as recommended by the Technology and Economic Assessment Panel, and take a final decision on such treatment at their Seventh Meeting;"(Decision VI/10)

The Parties requested the Technology and Economic Assessment Panel (TEAP):

> To identify uses of controlled substances as chemical process agents, to estimate emissions and ultimate fate, and to evaluate control technologies;
>
> To evaluate alternative process agents or technologies or products available to replace controlled substances in such uses; and to
>
> To report findings not later than March 1995. The Panel has asked the government of Sweden to organize and finance a special working group to complete this work.

1994 Nominations for Essential Uses

The Committee reviewed nominations from Austria, Belgium, Canada, Denmark, European Commission (EC), Finland, France, Germany, Greece, Ireland, Italy, Japan, Netherlands, Norway, Sweden, Switzerland, United Kingdom, and the United States. In all but laboratory and analytical uses and Space Shuttle rocket motor manufacturing the Committee was unable to recommend the nominations because there are technically and economically feasible alternatives and substitutes and/or because controlled substances are available in sufficient quantity and quality from existing sources. The

Committee also found that many requests were insufficiently supported with technical data.

HCFC

Few large scale current uses of HCFCs have been reported for solvents, coatings, or adhesives. In the near term HCFCs may be necessary as transition substances in some limited and unique applications including:

- cleaning delicate materials such as cultural heritage and archival property
- cleaning assemblies or components with sensitive materials or particular soils
- cleaning certain oxygen systems
- cleaning where explosive or flammable conditions are possible
- as a carrier of oil in precision applications.

In countries where HCFCs are prohibited, enterprises may, in certain specific cases, select perfluorinated carbons (PFCs) as an adjunct to specialized cleaning systems. PFCs have extremely long atmospheric lifetimes and have potent global warming potentials (GWPs) and should therefore be avoided where possible.

The Committee does not recommend the use of HCFC-141b to replace 1,1,1-trichloroethane as a solvent. A recommendation is not possible because HCFC-141b has an ozone-depletion potential (ODP) comparable to 1,1,1-trichloroethane and is not technically suitable for many cleaning applications.

It is estimated that HCFC-141b and HCFC-225 together will not replace more than 1 percent of global CFC-113 uses unless HCFC-225 becomes a substitute for CFC-113 in dry cleaning, which could increase use to approximately 5 percent. In some countries with active HCFC sales efforts, approximately 5 percent of CFC-113 solvent use (excluding dry-cleaning which may increase use) may be replaced with HCFC-141b. It is estimated that HCFCs may replace 1-5 percent of 1986 CFC-113 and 1,1,1-trichloroethane use as transitional substances and where no alternatives or substitutes are currently available.

The Committee cautions that there may be essential uses of very small quantities of ozone-depleting solvents that are not yet identified by the Committee, national governments, product distributors, and possibly the manufacturers themselves. However, it is expected that these uses will be identified as the accelerated phaseout in the EU is implemented and as production is halted. Stockpiled and recycled sources may be adequate to supply these uses.

PRICE INCREASES AND SHORTAGES OF OZONE-DEPLETING SOLVENTS

CFC-113 is produced primarily as a solvent with certain amounts sold as a feedstock for production of HFC-134a and some plastics. When CFC-113 sales in solvent uses are halted in the EU in 1995, and in all developed countries by 1996, the market may not be sufficient for developed country manufacturers to supply developing country markets.

CFC-113 is currently manufactured in two developing countries -- China and India -- and production facilities in South Korea and Taiwan are believed to be currently inactive.

Since 1,1,1-trichloroethane is produced as a feedstock for HCFC-141b and HCFC-142b, it will be more readily available than CFC-113 after 1996 for export to developing countries for their domestic needs, subject to Protocol restrictions.

It is the consensus of the Solvent, Coatings and Adhesives Technical Options Committee that quality grades of CFC-113 and 1,1,1-trichloroethane will be in uncertain supply after 1996 and that it will be prudent for enterprises in developing countries to move quickly to reduce and eliminate dependence on these chemical substances when cost-effective options are available. European, Japanese, and U.S. chemical manufacturers, distributors, and customers may have residual chemical supplies produced under national Protocol quotas or under Basic Domestic Needs quotas that may be marketed to developing countries if sales are less than expected in their developed country markets. This oversupply is less likely in the United States where taxes on stored ozone-depleting substances discourage oversupply.

A variety of alternative substances and technologies are currently in use or under development to facilitate the phaseout of CFC-113 and 1,1,1-trichloroethane. These alternatives include no-clean technologies, aqueous and semi-aqueous cleaning, other hydrocarbon solvents, non-ozone-depleting chlorinated solvents, HCFCs, perfluorocarbons, and a growing number of non-solvent cleaning processes.

No-clean technologies represent the optimum alternative and have been applied in an increasingly large number of electronics manufacturing applications in recent years. Nevertheless, research and testing of no-clean manufacturing processes is ongoing in the hope of making them viable alternatives in a wider variety of uses. Second to no-clean with respect to environmental protection is aqueous or semi-aqueous cleaning. The major drawbacks of these alternatives may be high energy consumption and wastewater treatment costs, depending on the process, requirements, and legislation.

HCFCs, though their use is transitional, are important alternatives to CFC-113 and 1,1,1-trichloroethane solvent use in applications for which no other viable alternative exists. Because of their lower ozone-depletion potential (ODP), HCFCs with a short lifetime are preferred to those with longer lifetimes. The ODP of all HCFCs is lower than the ODP of CFC-113. However, HCFCs should be used as substitutes for 1,1,1-trichloroethane only if the ODP of the HCFC substitute is lower than 0.10 and if their emissions are controlled using the best available technology. In addition, the 1992 Copenhagen Amendments to the Montreal Protocol require that production and consumption of HCFCs, as defined in the Protocol (Annex III G. Article 2F of UNEP/OzL. Pro. 4/15), must be reduced by 99.5% by 2020 and completely phased out by 2030. Thus, HCFCs are a valid alternative in certain limited applications while other, long term alternatives are being developed.

SECTOR PROGRESS

Electronics Cleaning

The electronics industry, which was heavily dependent on ozone-depleting solvents until recently, is fortunate to have the widest range of substitute materials and processes available. There is no technical reason why any company, large or small, in a developed or developing nation, should not be able to move away from such solvents immediately. Economic considerations, reported in previous editions (UNEP 1989, 1991), have shown that most substitute processes for this industry are less costly to run and, most often, give improved technical quality. On the other hand, relatively large investment capital is sometimes required to obtain the required results and this could be an obstacle, especially for small companies manufacturing "hi-tech" electronics.

To substitute for CFC-113 in defluxing, there is a large choice of processes, equipment, and materials commercially available for production units of all sizes. Where there are no technical specifications that require post-solder cleaning, "no-clean" techniques are often the most economical. This technique is recommended where the reliability criteria can be met. Where cleaning is a requirement, the use of water-soluble chemistry has generally proved to be preferable to most other processes, although it is not a universal solution. There is an adequate choice of other techniques where neither of these can be applied.

The Solvents, Coating and Adhesives Technical Options Committee do not recommend the following processes in electronics manufacture for funding under the provisions of the Montreal Protocol Multilateral Fund:

- *HCFC-141b for defluxing printed circuits*
- *Vapour-phase reflow soldering*
- *Vapour-phase drying of heavy organic solvents using PFCs*
- *Vapour-phase drying of water using HFCs or PFCs.*

Precision Cleaning

Precision cleaning applications are characterized by the high level of cleanliness required to maintain low-clearance or high-reliability components in working order. They are used in a variety of manufacturing industries, such as in aerospace, microelectronics, automotive, and medical. Several factors define the applications where a precision cleaning process is required. Some of these factors are:

- high standards for the removal of particulates or organic residue
- components constructed of chemically-sensitive materials
- components with physical limitations, such as geometry or porosity, which limit the ability to remove entrapped fluids like water
- high-cost components or components requiring high-reliability

CFC-113 and 1,1,1-trichloroethane have evolved as the preferred solvent cleaning method in precision cleaning because of their chemical inertness, low toxicity, non-flammability, low surface tension, and low water solubility.

However, to eliminate CFC-113 and 1,1,1-trichloroethane use, a number of companies have tested and implemented alternative cleaning methods. Possible alternatives include solvent and non-solvent options. Solvent options include other organic solvents (such as alcohols and aliphatic hydrocarbons), perfluorocarbons, HCFCs and their blends, and aqueous and semi-aqueous cleaners. Non-solvent options include supercritical fluid cleaning, UV/Ozone cleaning, pressurized gases, and plasma cleaning. Solvent use may also be reduced by controlled planning of repetitive or multiple cleaning operations.

Metal Cleaning

Metal cleaning is a surface preparation process that removes organic compounds such as oils and greases, particulate matter, and inorganic soils from metal surfaces. Metal cleaning prepares parts for subsequent operations such as further machining and fabrication, electroplating, painting, coating, inspection, assembly, or packaging. Parts may be cleaned multiple times during the manufacturing process.

The control approaches available for metal cleaning operations include solvent conservation and recovery practices and the use of alternative cleaning such as solvent blends, aqueous cleaners, emulsion cleaners, mechanical cleaning, thermal vacuum de-oiling, and no-clean alternatives. Alternatives to CFC-113 and 1,1,1-trichloroethane must be selected and optimized for each application given the varying substrate materials, soils, cleanliness requirements, process specifications, and end uses encountered in metal cleaning.

Dry Cleaning

Dry cleaning enables the cleansing and reuse of fabrics that cannot be cleaned by alternative methods. The inherent environmental friendliness of restoring freshness to soiled articles and garments is matched by extreme efficiency in terms of solvent and energy use in the dry cleaning process itself. Organic solvents are used to clean fabrics because, unlike water, they do not distort some natural and synthetic fibres. Water cleaning of many materials can affect the stability of fabric, lining, and interlining and may cause stretching or shrinkage.

A number of solvents can be used as alternatives to CFC-113 and 1,1,1-trichloroethane in dry cleaning operations. Perchloroethylene, the most widely used dry cleaning solvent, has been used in this application for over 30 years, during which time the systems for its safe use have become highly developed. The flammability of petroleum solvents effectively precludes their use in shops, although with proper precautions, they can be a substitute for CFC-113 on many fabrics. Petroleum solvents include white spirit, Stoddard solvent, hydrocarbon solvents, isoparaffins, n-paraffin, etc. A number of HCFCs and HCFC blends are currently available commercially for use in solvent applications. These include HCFC-123, HCFC-141b, and HCFC-225. These HCFCs have good stability, appropriate solvency, and non-flammability and some HCFCs are suitable for cleaning those delicate fabrics that currently depend on CFC-113. It should be noted, however, that HCFCs are transitional alternatives subject to a phaseout under the Montreal Protocol by the year 2030. Other classes of chemicals such as isoparaffins, solvents derived from sugar cane, and hydrocarbon/surfactant blends are theoretically possible alternative dry cleaning solvents. More research, however, is necessary to determine their feasibility for dry cleaning.

Adhesives

1,1,1-Trichloroethane is used as an adhesive solvent because it is non-flammable, dries rapidly, does not contribute to local air pollution, and performs well in many applications, particularly foam bonding. The rubber binders used in 1,1,1-trichloroethane adhesives are soluble in other solvents, such as acetone, ethyl acetate, heptane, and toluene. Although there has been a general trend in the U.S. and Western European adhesives industries to replace organic solvent-based adhesives with solvent-free types, one alternative is to return to earlier solvent formulations.

Some adhesives use water, in lieu of organic solvents, as the primary solvent. Recent literature on water-based adhesives suggests that there is still much debate about the overall effectiveness of water-based adhesives for many end uses.

The Committee D-14 of the American Society for Testing and Materials (ASTM) defines a hot melt adhesive as one that is applied in a molten state and forms a bond upon cooling to a solid state. Hot melt Pressure-Sensitive Adhesives (PSAs) now compete with water-based acrylics in outdoor applications. They have been used on paper labels for indoor applications since 1978.

Radiation curing is a production technique for drying and curing adhesives through the use of radiant energy such as ultraviolet (UV), infrared (IR), electron beam (EB), gamma, and x-rays. Radiation cured adhesives are especially well adapted for pressure sensitive tapes. One drawback is that adhesive curing is only possible in the "line of sight" of the radiant energy.

One way to lower volatile organic compound (VOC) emissions when using solvent-based adhesives is to increase the percent solids in the formulation. High solids adhesives have good performance characteristics, including initial bond strength comparable to that of 30 percent solids adhesives in medium and high demand applications and can be applied using existing equipment at normal line speeds with minor modifications. In other application areas, such as bonding rubber assemblies, high solids adhesives have not been as successful.

One-part epoxies, urethanes, and natural resins are often supplied as powders that require heat to cure. Powders are only used for non-pressure-sensitive applications. One advantage of the powder form is that no mixing or metering is necessary. However, powders must be refrigerated to maximise shelf life.

Moisture cure adhesives and reactive liquids can be applied as 100 percent non-volatile solid and liquid systems. These adhesives are composed entirely of binding substances, modifiers, and fillers (i.e., they have no carrier or solvent). Moisture cure adhesives cure upon exposure to the humidity in the ambient air; this type of adhesive requires application in a humid environment and might not work well in dry climates. Some two-component adhesives use reactive solvents which form part of the cured mass and thus do not depend on evaporation. In use, one solution consisting of an elastomer colloidally dispersed in a monomer is cured by a second solution through a free radical chemical polymerisation, thereby creating the bond .

Coatings and Inks

1,1,1-Trichloroethane is used by manufacturers, printers, and users of protective and decorative coatings and inks. CFC-113 use in the production of coatings or inks is negligible. In coatings, 1,1,1-trichloroethane is used alone or combined with other solvents to solubilize the binding substance which is usually composed of resin systems such as alkyd, acrylic, vinyl, polyurethane, silicone, and nitrocellulose resin. Inks are used to print items ranging from wallpaper to dog food bags to beverage bottles and cartons. Many of these uses involve the application of coloured ink to a film (or laminate) in the flexible packaging industry.

Some coatings contain water rather than organic solvents. Recent advances in water-based coating technology have improved the dry-time, durability, stability, adhesion, and application of water-based coatings. Primary uses of these coatings include furniture, electronics in automobiles, aluminum siding, hardboard, metal containers, appliances, structured steel, and heavy equipment. Water-based inks for flexographic and rotogravure laminates have been successfully developed and have overcome technical hurdles such as substrate wetting, adhesion, colour stability, and productivity.

Although high-solid coatings resemble conventional solvent coatings in appearance and use, high-solid coatings contain less solvent and a greater percentage of resin. High-solid coatings are currently used for appliances, metal furniture, and a variety of construction equipment. The finish of high-solid coatings is often superior to that of solvent-based coatings, despite the fact that high-solid coatings require much less solvent than do solvent-based coatings.

Powder coatings contain the resin only in powder form and thus have no solvent. While powder coatings were first used only for electrical transformer covers, they are now used in a large number of applications, including underground pipes, appliances, and automobiles.

Ultraviolet light/Electron beam (UV/EB)-cured coatings and inks have been used in very limited applications over the last 20 years, but their use has seen a dramatic increase in recent years. Several of the markets in which UV/EB-cured coatings and inks have been used more frequently in recent years are flexographic inks and coatings, wood furniture and cabinets, and automotive applications. One major limitation to the use of UV/EB-cured coatings and inks is outdoor durability. This is an especially important consideration in automotive applications.

Aerosols Solvent Products

1,1,1-Trichloroethane functions as either an active ingredient (e.g., degreaser or cleaner) or as a solvent in aerosol product formulations. Though most of the aerosol applications traditionally used 1,1,1-trichloroethane as their solvent, there are a small number of products which made use of CFC-113 as well. Most aerosol products currently employing CFC-113 and 1,1,1-trichloroethane can be reformulated with alternative compounds. Except for water, some HCFCs, and non-ozone-depleting chlorinated solvents (e.g., trichloroethylene, perchloroethylene, methylene chloride), all of the substitute solvents currently available are more flammable than 1,1,1-trichloroethane. The flammability is also a function of the propellant; butane and propane being more flammable than carbon dioxide, nitrous oxide or the traditional CFC-11/CFC-12 mixture.

Alternative solvents currently exist for virtually all aerosol solvent applications of CFC-113 and 1,1,1-trichloroethane. However, while some of these alternatives are functional, they are considered to be less than optimal for a variety of reasons. For example, in applications where a strong solvent is required, but the use of a flammable solvent would pose serious safety risks, substitutes may include only HFCs, HCFCs, and chlorinated solvents. While these solvents would be functional, HCFCs contribute to ozone-depletion, and chlorinated solvents are toxic and may pose health risks to workers and users of a product.

CFC-113 and 1,1,1-trichloroethane use in aerosols can also be reduced if alternative means of delivering the product are developed. Two examples of these alternative methods are: (1) a manual "wet-brush" (recirculating liquid) system, as a substitute for aerosol brake cleaners used in repair shops, and (2) increased use of professional dry cleaning services as a substitute for the use of aerosol spot removers.

Other Solvent Uses of CFC-113, 1,1,1-Trichloroethane, and Carbon Tetrachloride

Some amount, in most cases relatively small quantities, of CFC-113, 1,1,1-trichloroethane, and carbon tetrachloride are employed in a number of industry and laboratory applications. The application areas include drying of components, film cleaning, fabric protection, manufacture of solid rockets, laboratory testing and analyses, process solvents, semiconductor manufacturing, and others.

The Committee consensus is that by 1996, in accordance with the Montreal Protocol, most of the CFC-113, 1,1,1-trichloroethane, and carbon tetrachloride used for these applications can be replaced by the alternatives.

In the applications of laboratory analyses and in the manufacture of a specific large scale solid rocket motor, the Parties have granted an exemption for continued use of specified ozone-depleting solvents for 1996 and 1997. The exemptions are subject to review and alternatives are being investigated.

In the case of use of ozone-depleting substances as process chemicals, there are also a number of alternatives identified in this report. In addition, an in-depth review of alternatives is planned for completion and presentation by the Technical and Economic Assessment Panel to the Parties by early 1995.

PROGRESS IN ELIMINATING ODS FROM ROCKET MOTORS

Ozone Depleting Substances (ODSs) have been routinely used globally for decades in the manufacture of space launch vehicle solid rocket motors (SRMs). The primarily ozone-depleting solvents used are 1,1,1-trichloroethane (TCA or methyl chloroform) and CFC-113. These substances are used because of their excellent cleaning properties, low toxicity, chemical stability and non-flammability.

In the United States, large solid rocket motors (SRMs) are used to launch into space communication, navigational and scientific satellites and the manned Space Shuttle orbiters. Large SRMs include the existing Titan IV SRM as well as its upgraded version called the SRMU and the Space Shuttle redesigned solid rocket motor (RSRM).

Despite these technical safety and reliability challenges, the SRM industry has successfully tested, approved, and implemented significant ODS elimination. Since 1989, the four US manufacturers of large SRMs have eliminated over 1.6 million pounds of ODS use per year. Current (1994) ODS usage is less than 48 percent of the use in 1989. Usage in 1995 is estimated to be less than 22 percent of 1989, and manufacturers have committed to complete elimination of ODSs within the next few years.

Update on the Essential Use Applications

NASA/Thiokol was granted an essential use production exemption for 1996 and 1997. NASA/Thiokol have proceeded with their phaseout and are ahead of schedule for eliminating non-essential uses and investigating additional alternatives and substitutes. However, at this time NASA/Thiokol has not identified any acceptable substitutes that would reduce their essential use below the previously calculated amounts.

The Solvents, Coatings, and Adhesives TOC reported in the March 1994 Report that it was likely that all manufacturers of solid rocket motors use ODSs. The Committee has confirmed that other U.S. and European solid rocket motors use these substances and that these organizations are expected to nominate additional essential uses by January 1, 1995 for decision in 1995.

The U.S. Titan program is working to completely eliminate the use of ODSs and has invested substantial resources in successfully developing alternatives to ODS use. The prime contractor and the major manufacturers of Titan IV vehicle components will reduce all ODS use by 99 percent, from 1.33 million kg in 1989 to 9,200 kg in 1996. Four small-quantity ODS uses are critical to the success of the Titan SRMU. These are (1) surface preparation to ensure effective bonding of the internal insulator to the composite case, (2) surface preparation to ensure effective attachment of breather cloth to the insulator to permit uniform curing, (3) surface preparation to ensure effective bonding of the propellant to the insulator, and (4) dispersing propellant cure catalyst during propellant mixing. The quantity of ODS necessary to complete SRMU manufacture for the final nine flight sets is 3,660 kg per year or less for 1996 through to 1999.

Both CFC-113 and TCA are used in the European Ariane Espace Programme. Efforts to find substitutes for these programmes concern CRYOSPACE for liquid rocket engines and Societe Europeénne de Propulsion (S.E.P.) for solid motors.

The Japanese space rocket industry currently uses CFC-113 and TCA but expects to phase out the uses by the end of 1995. Latest achievements include the solid rocket booster (SRB) for the H-II launch vehicle which is capable of launching a 2 Ton satellite to Geosynchronous orbit.

Cleaning of Oxygen Systems

In January 1994 NATO identified the cleaning of oxygen systems as one of the most difficult challenge facing military and aerospace applications. In Fall 1994, the International Cooperative for Ozone Layer Protection (ICOLP), Aerospace Industry Association (AIA), U.S. EPA, National Aeronautical and Space Administration (NASA) and the U.S. Air Force convened a special workshop on cleaning of oxygen systems without ozone-depleting solvents.

Oxygen systems include: life support systems such as diving, totally encapsulated suits, emergency breathing devices, fire & rescue backpacks, submarine, aircraft, manned spacecraft, and medical applications; propulsion systems such as liquid rocket motors; industrial systems such as chemical production; and other unique systems and customer products such as welding equipment.

Oxygen systems must be kept clean because organic compound contamination, such as hydrocarbon oil, can ignite easily and provide a kindling chain to ignite surrounding materials. Contamination can also consist of particles that could ignite or cause ignition when impacting other parts of the system. Risk is increased by the typical proximity of oxygen systems to very large quantities of fuel materials, and the common necessity of locating oxygen systems in confined spaces with difficult or impossible access and egress (e.g. space ships, submarines, aircraft, and surface ships).

Examples of the challenges presented by these applications include the cleaning of the space shuttle external fuel tank, cleaning of aircraft carrier liquid oxygen plants, cleaning of installed submarine and transport aircraft high pressure oxygen systems, and the gauges and instrumentation associated with each. Examples of devices typically cleaned in these systems include tubing, gauges, regulators, valves, and metering devices. It is usually most effective to clean oxygen equipment at the piece part level in a proper facility. It is more difficult to clean oxygen equipment in aircraft and ship equipment in place with difficult accessibility and temperature extremes. Additional challenges occur in many other industrial oxygen systems such as those used in production and transfer of both gaseous and liquid oxygen, in medical applications, and in welding. Cleaning of equipment used in the oxygen production industry involves unique challenges such as compatibility with aluminum heat exchangers.

Solvents such as non-ozone depleting chlorinated solvents and hydrocarbons often clean satisfactorily, but all have environmental or toxicity concerns, and some have flammability concerns.

Aqueous cleaning options have been successfully developed and implemented for many oxygen system cleaning situations. For example, Lockheed uses aqueous processes in the manufacturing and maintenance of aircraft and missile oxygen systems, the Air Force uses aqueous cleaning for some aircraft oxygen system maintenance, NASA/Kennedy Space Center uses aqueous solutions for cleaning oxygen bulk storage and transfer systems for rocket motors, and the U.S. Navy uses aqueous cleaning processes for cleaning the tubing in oxygen systems on ships and submarines.

Isopropyl alcohol (IPA) is being used by Lufthansa German Airlines to clean the oxygen systems in their commercial aircraft fleet. Sweden has reported using a solvent blend for oxygen system cleaning consisting of 95% ethanol.

Some parts of oxygen systems can be changed to simplify or avoid the necessity of cleaning or they can be adapted to allow aqueous cleaning.

Some oxygen system components still depend on CFC or chlorinated solvent cleaning because current alternatives and substitutes are not technically suitable. In other cases, rigid specifications and requirements may need to be changed from prescriptive to performance standards to allow technically feasible solutions to be used.

This Report includes case studies of successful elimination of ozone-depleting solvents which discuss the evaluation and implementation of materials, alternative technologies, and processes. The following are included in Chapter 11: Allied Signal (evaluation of aqueous saponifiers), AT&T Bell Labs (non-ODS alternatives including no-clean soldering), Beck Electronics (alternative solvents and design of cleaning equipment), Ford Motor Company (no-clean soldering), Hitachi (non-ODS alternatives), Honeywell (non-ODS alternatives), IBM Corporation (no-clean soldering), Japan Industrial Conference on Cleaning (information dissemination), Lockheed Sanders Company (company phaseout efforts), Miljoministeriet (hydrocarbon dry cleaning), Minebea Company (aqueous cleaning of ball bearings), National Semiconductor (company phaseout efforts), Naval Aviation Depot Cherry Point (hand-wipe cleaning), Northern Telecom (company phaseout efforts), Robert Bosch Corporation (aqueous cleaning), Rockwell International (low-residue flux), Seiko Epson Corporation (alternatives to ODSs), Singapore Institute of Standards and Industrial Research (ODS-free certification of businesses), Swedish EPA (country-wide phaseout efforts), Toshiba Corporation (vinyl-copolymer masking agent), U.S. Air Force Aerospace Guidance and Metrology Center (aqueous & non-aqueous alternatives), Vibro-Meter, SA (water-based cleaning).

Total Equivalent Warming Impact (TEWI)

Total Equivalent Warming Impact (TEWI) provides an important tool in the selection procedure for alternative cleaning and drying technologies. However, TEWI must not be the only criterion when selecting the cleaning, drying, or other technology for a manufacturing process. The Alternative Fluorocarbons Environmental Acceptability Study (AFEAS) has provided a methodology to calculate TEWI for wide range of available systems.

The selection of the best technology to displace CFC-113 or 1,1,1-trichloroethane (methyl chloroform) must be specific to the intended applications and will represent a trade-off or balancing of several key parameters: worker safety (toxicity or flammability concerns), investment, operating costs, energy efficiency and reliability. It must also consider a series of environmental issues (discharges to water or landfill, local environmental air quality (smog) and global impact).

This report has evaluated one of the selection parameters, TEWI, for a number of systems. A summary of the key findings follows.

- Solvent losses from the cleaning equipment are potentially lower than assumed in the 1991 study, resulting in lower calculated contributions to TEWI. This reduction in emissions is possible through the adoption of enhanced vapor recovery and improved/novel approaches to materials handling (e.g., freeboard dwell). In some cases, the above technologies can be retrofitted to very modern existing equipment, with results almost comparable to new equipment. However, such equipment will require careful operation and maintenance to sustain low emission rates.

- The no-clean systems used for the manufacture of printed wire assemblies have the potential for the lowest TEWI. For metal cleaning, chlorocarbon-based systems (e.g., PCE, TCE) have the potentially lowest TEWI. However, these chlorinated solvent systems may be subject to various national, regional and/or local regulations or emission limits that may severely limit the use of these chemicals for cleaning applications.

- The PFC system studied has the highest TEWI.

- While they use more energy per unit of work (throughput), aqueous, semi-aqueous and alcohol systems generally have been shown to have a lower TEWI than HCFC and HFC-based systems because emissions from aqueous, semi-aqueous, and alcohol systems do not contribute to global warming.

- In the case of HCFC/HFC/PFC-based systems, the direct effect caused by emission of the chemical, represents from 40 percent to over 90 percent of the calculated contribution to potential global warming.

Future study should assess the effects of variations in equipment and practices on TEWI and estimate implementation time for alternative systems in developing countries.

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

In response to the growing scientific consensus that chlorofluorocarbons (CFCs) and halons would ultimately deplete the ozone layer, the United Nations Environment Programme (UNEP) in 1981 began negotiations to develop multilateral policies for protecting the ozone layer. These negotiations resulted in the Vienna Convention for the Protection of the Ozone Layer in March 1985. The convention provided a framework for international cooperation in research, systematic observation, and information exchange. In September 1987, 24 nations including the United States, Japan, the Soviet Union, and members of the European Community signed the Montreal Protocol on Substances That Deplete the Ozone Layer (hereafter referred to as "the protocol"). As of February 1994, 132 nations and the European Community had ratified the Protocol (see Table I-1). These countries represent virtually all of the world's consumption[1] of CFCs and halons. The Protocol, which entered into force on January 1, 1989, limited consumption of specified CFCs to 50 percent of 1986 levels by the year 1998 and called for a production freeze of specified halons at 1986 levels starting in 1992. Table I-2 lists CFCs, halons, and other substances controlled under the Protocol.

Shortly after the 1987 Protocol was negotiated, new scientific evidence conclusively linked CFCs to depletion of the ozone layer and indicated that depletion had already occurred. Consequently, many countries called for further actions to protect the ozone layer by expanding and strengthening the control measures of the 1987 Montreal Protocol. In June 1990, the Parties to the Montreal Protocol met in London and agreed to Protocol adjustments requiring more stringent control measures on the CFCs and halons than those listed in the original agreement. Amendments placed further control measures on other ozone-depleting substances including carbon tetrachloride and 1,1,1-trichloroethane. In April 1991 the National Aeronautics and Space Administration (NASA) concluded that depletion of the ozone layer over the past decade has occurred at a rate faster than previously estimated. The four to five percent depletion over populated northern latitudes since 1978 led many countries to propose more stringent phase-out schedules than those proposed at the London meeting of the Parties to the Protocol. As a result, the Parties to the Protocol met in Copenhagen in November 1992 and agreed to further amendments and adjustments requiring even more stringent control measures on all controlled substances. In addition, the Parties added methyl bromide to the list of controlled substances and agreed to freeze production of methyl bromide at 1991 levels by January 1, 1995. The reduction schedules

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[1] Consumption is equal to production plus imports minus exports.

Table I-1. PARTIES TO THE MONTREAL PROTOCOL

- Algeria
- Antigua and Barbuda
- Argentina
- Australia
- Austria
- Bahamas
- Bahrain
- Bangladesh
- Barbados
- Belarus
- Belgium
- Benin
- Bosnia/Herzegovina
- Botswana
- Brazil
- Brunei Darussalam
- Bulgaria
- Burkina Faso
- Cameroon
- Canada
- Central African Republic
- Chile
- China
- Colombia
- Congo
- Costa Rica
- Cote d'Ivoire
- Croatia
- Cuba
- Cyprus
- Czech Republic
- Denmark
- Dominica
- Ecuador
- Egypt
- El Salvador
- EEC
- Fiji
- Finland
- France
- Gambia
- Germany
- Ghana
- Greece
- Grenada
- Guatemala
- Guinea
- Guyana
- Honduras
- Hungary
- Iceland
- India
- Indonesia
- Iran
- Ireland
- Israel
- Italy
- Jamaica
- Japan
- Jordan
- Kenya
- Kiribati
- Kuwait
- Lebanon
- Libyan Arab Jamahiriya
- Liechtenstein
- Luxembourg
- Malawi
- Malaysia
- Maldives
- Malta
- Marshall Islands
- Mauritius
- Mexico
- Monaco
- Morocco
- Myanmar
- Namibia
- Netherlands
- New Zealand
- Nicaragua
- Niger
- Nigeria
- Norway
- Pakistan
- Panama
- Papua New Guinea
- Paraguay
- Peru
- Philippines
- Poland
- Portugal
- Romania
- Republic of Korea
- Russian Federation
- St. Kitts and Nevis
- St. Lucia
- Samoa
- Saudi Arabia
- Senegal
- Seychelles
- Singapore
- Slovakia
- Slovenia
- Solomon Islands
- South Africa
- Spain
- Sri Lanka
- Sudan
- Swaziland
- Sweden
- Switzerland
- Syrian Arab Republic
- Tanzania
- Thailand
- Togo
- Trinidad & Tobago
- Tunisia
- Turkey
- Turkmenistan
- Tuvalu
- Uganda
- Ukraine
- United Arab Emirates
- United Kingdom
- United States
- Uruguay
- Uzbekistan
- Venezuela
- Viet Nam
- Yugoslavia
- Zambia
- Zimbabwe

Date: February 1994

Table I-2. SUBSTANCES CONTROLLED BY THE MONTREAL PROTOCOL

		ODP Relative to CFC-11
	ANNEXE A	
Group I:		
CFC-11	Trichlorofluoromethane	1.0
CFC-12	Dichlorodifluoromethane	1.0
CFC-113	1,1,2-Trichloro-1,2,2-trifluoroethane	0.8
CFC-114	1,2-Dichlorotetrafluoroethane	1.0
CFC-115	Chloropentafluoroethane	0.6
Group II:		
Halon-1211	Bromochlorodifluoromethane	3.0
Halon-1301	Bromotrifluoromethane	10.0
Halon-2402	Dibromotetrafluoroethane	6.0
	ANNEXE B	
Group I:		
CFC-13	Chlorotrifluoromethane	1.0
CFC-111	Pentachlorofluoroethane	1.0
CFC-112	Tetrachlorodifluoroethane	1.0
CFC-211	Heptachlorofluoropropane	1.0
CFC-212	Hexachlorodifluoropropane	1.0
CFC-213	Pentachlorotrifluoropropane	1.0
CFC-214	Tetrachlorotetrafluoropropane	1.0
CFC-215	Trichloropentafluoropropane	1.0
CFC-216	Dichlorohexafluoropropane	1.0
CFC-217	Chloroheptafluoropropane	1.0
Group II:		
CCl_4	Carbon Tetrachloride (tetrachloromethane)	1.1
Group III:		
1,1,1-Trichloroethane	Methyl Chloroform (1,1,1-Trichloroethane)	0.1

ANNEXE C

Partially halogenated fluorocarbons (including HCFC-22, HCFC-123, HCFC-141, and HCFC-225), are defined as transitional substances by the Montreal Protocol under Annexe C.

ANNEXE E

Group I:		
CH_3Br	Methyl Bromide	0.7

Source: Montreal Protocol on Substances that Deplete the Ozone Layer set out in the Montreal Protocol Copenhagen Amendments of 1992 are shown in Table I-3.

Table I-4 compares worldwide consumption and ozone-depletion potentials of CFC-11, CFC-12, CFC-113, CFC-114, and CFC-115. Worldwide consumption of 1,1,1-trichloroethane in 1988 and 1990 was 679,000 MT, and 726,000 MT, respectively (Midgeley 1991). The 1988 consumption of 1,1,1-trichloroethane in the U.S, Western Europe, and Japan was estimated at 582,000 MT (Chem Systems 1989). It has been estimated that of this amount, approximately 100,000 MT of 1,1,1-trichloroethane were used outside W. Europe, Japan, and the U.S. (Chem Systems 1989). Figure I-1 presents the breakdown of 1,1,1,-trichloroethane consumption in these three regions.

1.2 TERMS OF REFERENCE FOR THE COMMITTEE[2]

The June 1990 London Meeting of Parties to the Montreal Protocol reconvened the 1989 UNEP assessment panels. The 1989 UNEP assessment panels consisted of the scientific assessment, the environmental effects assessment, the technology assessment, and the economics assessment panels. The technical and economics panels were combined for the 1991 Assessment. The three international assessment panels were requested to report on:

- the science of stratospheric ozone-depletion
- the environmental and public health effects of stratospheric ozone-depletion
- the technical feasibility and earliest possible date, in each of the major use sectors, for phasing out production of ozone-depleting substances and the related anticipated economic concerns. The 1991 Technical and Economic Assessment Panel is divided into six Committees:
  - UNEP Aerosols, Sterilants, Miscellaneous Uses and Carbon Tetrachloride Technical Options Committee
  - UNEP Economic Options Committee
  - UNEP Halons Technical Options Committee
  - UNEP Refrigeration Options Committee
  - UNEP Solvents, Coatings and Adhesives Technical Options Committee
  - UNEP Technical Options Committee for Foams

The third meeting of the Parties to the Protocol in Nairobi in June 1991 requested the assessment panels, particularly the Technology Assessment Panels to:

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[2] This section addresses Decision II-13 Assessment Panels of the Second Meeting of the Parties to the Montreal Protocol, Decision III-12 Assessment Panels and Decision III-8 Trade Names of Controlled Substances of the Third Meeting of the Parties to the Protocol (Kurita 1991b), and Decisions IV-13 and IV-23 of the Fourth Meeting of the Parties to the Protocol.

Table I-3: SUMMARY OF COPENHAGEN AMENDMENTS TO THE MONTREAL PROTOCOL

Chlorofluorocarbons (Group I - Annexe A: CFC-11, CFC-12, CFC-113, CFC-114, CFC-115)

- Freeze at 1986 levels by July 1989
- 75 percent reduction from 1986 levels by January 1994
- 100 percent reduction from 1986 levels by January 1996

Other fully halogenated CFCs (Group I - Annexe B: CFC-13, CFC-111, CFC-112, CFC-211, CFC-212, CFC-213, CFC-214, CFC-215, CFC-216, CFC-217)

- 20 percent reduction from 1989 levels by January 1993
- 75 percent reduction from 1989 levels by January 1994
- 100 percent reduction from 1989 levels by January 1996

Halons (Group II - Annexe A: Halon-1211, Halon 1301, Halon-2402)

- Freeze at 1986 levels by January 1992
- 100 percent reduction from 1986 levels by January 1994

1,1,1-Trichloroethane (Group III - Annexe B)

- Freeze at 1989 levels by January 1993
- 50 percent reduction from 1989 levels by January 1994
- 100 percent reduction from 1989 levels by January 1996

Carbon Tetrachloride (Group II - Annexe B)

- 85 percent reduction from 1989 levels by January 1995
- 100 percent reduction from 1989 levels by January 1996

Partially Halogenated Fluorocarbons (Group I - Annexe C)

- Freeze at specified level by January 1996 (specified level is equal to 3.1% of 1989 consumption of Group I Annexe A controlled substances **plus** 100% of 1989 consumption of Group I Annexe C controlled substances)
- 35 percent reduction from level of freeze by January 2004
- 65 percent reduction from level of freeze by January 2010
- 90 percent reduction from level of freeze by January 2015
- 99.5 percent reduction from level of freeze by January 2020
- 100 percent reduction from level of freeze by January 2030

Methyl Bromide (Group I - Annexe E)

- Freeze at 1991 levels by January 1995

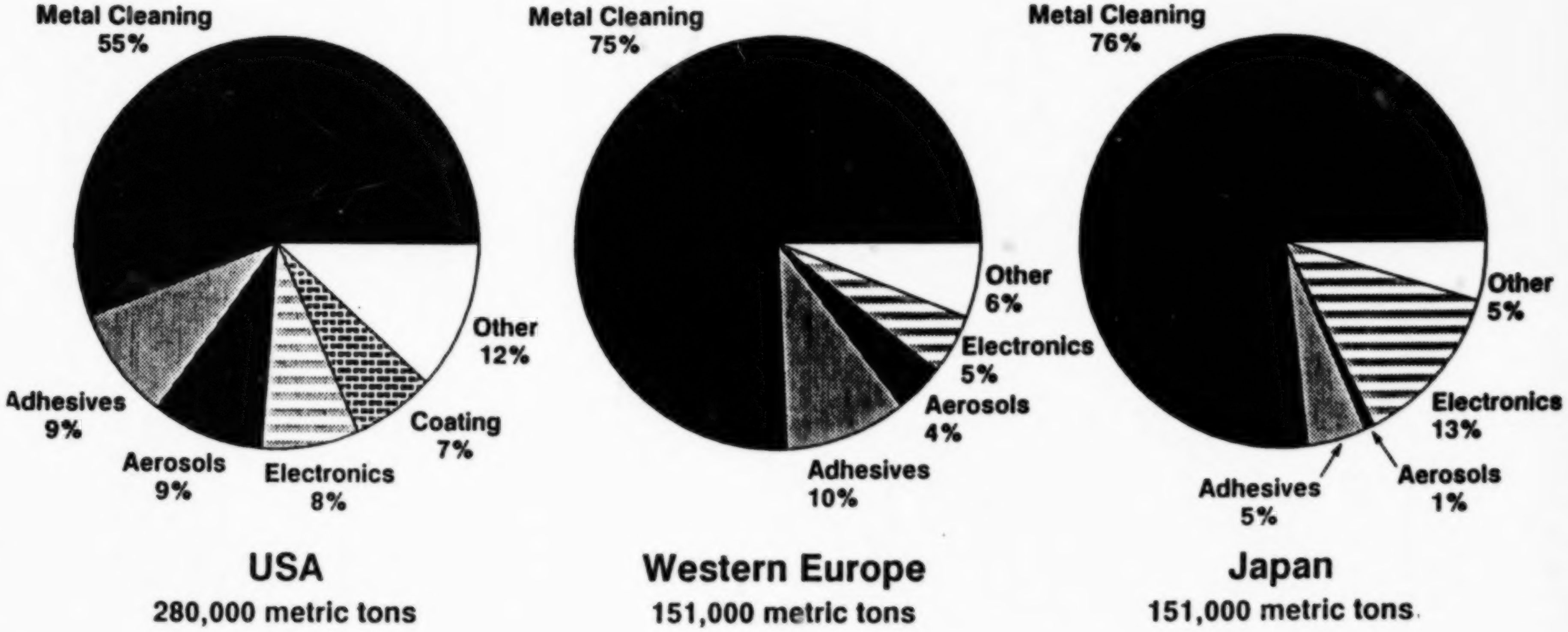
Table I-4. COMPARISON OF WORLDWIDE CONSUMPTION OF CONTROLLED CFCS AND OZONE-DEPLETING POTENTIAL (ODP)

	1986 Worldwide Consumption (kilotonnes)	Percent of Basket	Relative Total ODP	Percent ODP of Basket	Atmospheric Lifetime (years)
CFC-11	370	35.0	1.00	36.4	75
CFC-12	480	45.4	1.00	47.2	111
CFC-113	178	16.8	0.80	14.0	90
CFC-114	15	1.4	1.00	1.5	-
CFC-115	15	1.4	0.60	0.9	-

Source: Montreal Protocol on Substances that Deplete the Ozone Layer

Figure 1-1

BREAKDOWN OF 1,1,1-TRICHLOROETHANE CONSUMPTION IN THE U.S., WESTERN EUROPE, AND JAPAN



Source: Chem Systems 1989

- "evaluate, without prejudice to Article 5 of the Montreal Protocol, the implications, in particular for developing countries, of the possibilities and difficulties of an earlier phase-out of the controlled substances, for example of the implications of a 1997 phase-out."

- "take into account the London Resolution on transitional Substances (Annexe VII to the report of the Second Meeting of the Parties to the Montreal Protocol), to identify the specific areas where transitional substances are required to facilitate the earliest possible phase-out of controlled substances, taking into account environmental, technological, and economic factors, where no other more environmentally suitable alternatives are available. The quantities likely to be needed for those areas and for those areas of application currently served by transitional substances shall both be assessed."

- "request the assessment panels to identify the transitional substances with the lowest potential for ozone-depletion required for those areas and suggest, if possible, a technically and economically feasible timetable, indicating associated costs, for the elimination of transitional substances."

- ".....submit...reports in time for their consideration by the Open-Ended Working Group with a view to their submission for consideration by the Fourth Meeting of the Parties."

Most recently, the fourth meeting of the Parties to the Protocol, held in Copenhagen in November 1992, requested the following activities of the assessment panels:

- "request the Technology and Economic Assessment Panel and its Technical and Economic Options Committees to report annually to the Open-Ended Working Group of the Parties to Montreal Protocol the technical progress in reducing the use and emissions of controlled substances and assess the use of alternatives, particularly their direct and indirect global-warming effects."

- "request the three assessment panels to update their reports and submit them to the Secretariat by 30 November 1994 . . . These assessments should cover all major facets discussed in the 1991 assessments with enhanced emphasis on methyl bromide. The scientific assessment should also include an evaluation of the impact of sub-sonic aircraft on ozone."

- "encourage the panels to meet once a year . . ."

To assure the widest possible international participation in the review and the subsequent report, the 1994 Assessment Panels consist of some members of the 1989 and 1991 UNEP Assessment Panels and additional new experts nominated by Governments. Not only were experts from industry, government, academic institutions, and nongovernmental organizations invited to prepare a comprehensive and technically specific "Control Options Report" for each sector, but the chairpersons of the UNEP Technical and Economics Panel and each of the Technical and Economics Option Committee also contacted countries to encourage their active participation in this review process. By contacting producers, manufacturers, and trade associations and by arranging for additional technical input, the chairpersons of the Technical and Economic Option Committee further insured widespread participation in preparing the Technical Options Report on Solvents, Coatings, and Adhesives. As with the 1989 and 1991 reports, the 1994 report has undergone extensive peer review and will be distributed internationally by UNEP.

The member countries of the Committee included representatives from North American, Latin American, European, African, and Asian governments and companies (see Table I-5). Affiliations of the committee members are listed in Table I-6. In addition, the Committee had the benefit of advice from a distinguished panel of worldwide experts which included representatives of government agencies, chemical producers, and industry associations (see Table I-7). Committee meetings during the preparation of the 1991 report were held in Germany, Japan, Mexico, Sweden, Switzerland, Thailand, United Kingdom, and the United States to facilitate participation by interested organizations. These meetings enabled Committee members to gather information first hand on the potential for substitution of CFC-113 and 1,1,1-trichloroethane and on the progress made to date. The Committee met with a number of companies, trade associations, and government agencies to understand their position on this issue.

1.3 BASIS FOR COMMITTEE RECOMMENDATIONS TO UNEP AND COMMITTEE POSITION ON CFC-113, 1,1,1-TRICHLOROETHANE AND PARTIALLY HALOGENATED FLUOROCARBONS

The Committee's recommendations to the UNEP are the consensus of the Committee. New scientific information suggests that ozone depletion is occurring at a rapid rate. The levels of future chlorine and bromine concentrations in the upper atmosphere will depend primarily on future emissions of CFCs, 1,1,1-trichloroethane, halons, HCFCs, halothanes, and other ozone-depleting substances.

In August 1988, the U.S. Environmental Protection Agency (EPA) issued a study entitled "Future Concentrations of Stratospheric Chlorine and Bromine"[3] which looked at chlorine and bromine levels after the implementation of the restrictions in the Montreal Protocol. The U.S. EPA predicted that, based on their growth scenarios, levels of chlorine in the stratosphere would increase from 2.7 to 8 parts per billion (ppb) by 2075, even with the reductions in CFC production called for in the Protocol. This increase would be caused not only by the allowed use of CFCs and halons under the Protocol, but also by CFC use in countries that are not members of the Protocol and by the growth in the production and use of chemicals such as 1,1,1-trichloroethane and carbon tetrachloride. While reduction efforts under the Protocol, coupled with the greatly increased number of signatories, is likely to result in increases in stratospheric chlorine levels closer to the low end of this range, such increases are still of concern.

The second and third meetings of Parties to the Protocol in London and Nairobi called for an examination by the Committee of the technical

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[3] Clx Report, U.S. EPA Office of Air and Radiation, 400/1-88/005, August 1988.

Table I-5. MEMBER COUNTRIES OF THE UNEP SOLVENTS, COATINGS AND ADHESIVES TECHNICAL OPTIONS COMMITTEE

Member Countries
Belgium
Brazil
Canada
France
Germany
Japan
Jordan
Germany
Malaysia
Mexico
Singapore
Sweden
Switzerland
Thailand
United Kingdom
United States

Table I-6. ORGANIZATIONS WHOSE EMPLOYEES SERVE ON THE UNEP SOLVENTS, COATINGS, AND ADHESIVES TECHNICAL OPTIONS COMMITTEE

Member Organizations
Allied Signal Incorporated
Asahi Glass Company Ltd.
AT&T Bell Laboratories
Boeing Company
British Aerospace (Dynamics) Ltd.
Charles Stark Draper Laboratory
Digital Equipment Corporation
Dow Chemical - Advanced Cleaning Systems
European Chlorinated Solvents Association
Ford Motor Company
Friends of the Earth
GEC - Marconi
Global Centre for Process Change
Hitachi Ltd.
ICF Incorporated
IFC
ITT Teves GmbH
Japan Association for Hygiene of Chlorinated Solvents
Japan Audit and Certification Organisation Ltd.
JEMA
Lockheed
Lufthansa German Airlines
Mexican Chamber of Industries
Ministry of Planning - Jordan
National Semiconductor
OXITENO
Promosol
Protonique S.A.
SAEO South America Electronics Operation
Siemens AG
Singapore Institute of Standards and Industrial Research
Sketchley PLC
Swedish Environmental Protection Agency
TELEMECANIQUE
Texas Instruments Incorporated
Thai Airways International
U.S. Air Force
U.S. Environmental Protection Agency
Vulcan Chemicals
Waste Policy Institute

Table I-7. CORPORATE AND GOVERNMENT PRESENTATIONS IN MEETINGS HELD BY THE UNEP SOLVENTS, COATINGS, AND ADHESIVES TECHNICAL OPTIONS COMMITTEE

[1]Allied Signal,Inc., U.S.A.
[2]All Japan Laundry and Dry Cleaning Association, Japan
[2]Alpha Metals, Hong Kong
[2]Arakawa Chemical Industries, Ltd., Japan
[3]Asahi Glass Company, Ltd., Japan
[2]Asea Brown Boveri (ABB)
[2]Atsugi Unisia Corporation, Japan
[2]AT&T-Telecommunications Products (Thai) Ltd., Thailand
[2]Balzers A.G., Principality of Liechtenstein
[2]Berghof GmbH & Co., Germany
[3]Boeing Company, U.S.
[3]British Aerospace (Dynamics) Ltd., U.K.
[3]Brulin Corporation
[2]Canon, Inc., Japan
[2]Chemical Technology Research Co., Ltd., Japan
[2]Columbia Cement, Co., Inc.
[2]ConSolve, A.S., Norway
[3]Daikin Industries, Japan
[2]Dan Science Co., Ltd., Japan
[2]Data General, Thailand
[3]Deft Corporation
[2]Department of Industrial Works - Ministry of Industry, Thailand
[2]Digital Equipment Corporation, Singapore
[2]Dow Chemical, Germany, Switzerland
[2]Du Pont Electronics, U.K.
[3]Du Pont, Japan, U.K., and U.S.A.
[2]Durr GmbH, Germany
[1]Ensambles Magneticos, S.A., Mexico
[2]Ericsson Electronics, Sweden
[3]Exxon Chemicals, Canada
[2]Fujitsu Ltd., Japan
[2]FFV Aerotech, Sweden
[2]GEC Research, U.K.
[2]General Dynamics, U.S.A.
[1]Halogenated Solvents Industry Alliance, U.S.A.
[2]Hitachi Chemical Techno-Plant Co., Ltd., Japan
[2]Hitachi, Ltd., Japan
[2]Hitachi Construction Machinery Co., Ltd., Japan
[2]IBM, Sweden
[3]ICI PLC Chemicals and Polymers Ltd., U.K.
[2]International Institute for Energy Conservation, Asia Office, Thailand
[2]ITT Teves Gmbh, Germany
[2]Japan Alcohol Association, Japan
[2]Japan Electrical Manufacturers' Assn., Japan
[2]Karl Roll GmbH, Germany
[2]Koki Company, Ltd., Japan
[2]Kolb GmbH & Co., Germany
[2]Leica Heerbrugg, Switzerland
[3]LPS Laboratories, U.S.
[2]Matsushita Refrigeration Co., Japan
[2]Micropolis Corporation, Thailand
[2]Minebea Group, Thailand
[1]Ministry of International Trade and Industry, Japan
[2]Mitsubishi Electric Corp., Japan

(continued on next page)

Table I-7. CORPORATE AND GOVERNMENT PRESENTATIONS IN MEETINGS HELD BY THE UNEP SOLVENTS, COATINGS, AND ADHESIVES TECHNICAL OPTIONS COMMITTEE (Continued)

[3]3M Corporation
[2]National Semiconductor, Thailand
[2]National Research Institute for Pollution and Resources, MITI, Japan
[1]NEC, Japan
[2]Nippondenso Company, Ltd., Japan
[2]Nissan Motor Co., Ltd., Japan
[2]Nissin Electric, Japan
[1]Northern Telecom, U.S.A. and Canada
[2]NTN Corporation, Japan
[1]Plamex S.A., Mexico
[2]SAAB Scania, Sweden
[4]SAGEM, France
[1]SEHO, Germany
[1]Seiko-Epson, Japan
[2]Semiconductor Ventures International, Thailand
[2]Senju Metal Industry Co., Ltd, Japan
[1]Separation Technologists, U.S.A.
[1]Sharp Corporation, Japan
[2]Siam Compressor Industry Co., Ltd., Thailand
[3]Siemens, Germany
[2]Siemens-Elema, Sweden
[1]Sigma Industries, U.S.A.
[2]Swedish Institute for Production Engineering Research, Sweden
[2]Tinker Air Force Base, U.S.A.
[3]Toshiba Corporation, Japan
[2]Toshiba Display Devices (Thailand) Co., Ltd., Thailand
[4]Thiokol Corporation, U.S.A.
[2]ULVAC Ltd., Japan
[1]United States Air Force Engineering Services Center, Tyndall Air Force Base, U.S.A.
[2]VCI, Germany
[2]VOLVO Aero Support
[3]W.R. Grace, U.S.
[2]ZVEI, Germany

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[1] 1989 Presentation.
[2] 1991 Presentation.
[3] 1989 and 1991 Presentations.
[4] 1994 Presentations.

feasibility of using only alternatives which do not deplete the ozone layer. In the short-term some might use other low ODP alternatives. Figure I-2 compares the ODP of CFC-113 and 1,1,1-trichloroethane with that of the new HCFCs and HFCs currently in use or under development. The Committee believes that there are a wide variety of alternatives that can completely replace CFC-113 and 1,1,1-trichloroethane use.

A variety of alternative substances and technologies are currently under development to facilitate the phaseout of CFC-113 and 1,1,1-trichloroethane. These alternatives include aqueous and semi-aqueous cleaning, alcohol mixtures, other hydrocarbon solvents, HCFCs, perfluorocarbons, no-clean technologies, and a growing number of non-solvent cleaning processes.

No-clean technologies represent the optimum alternative and have been applied in an increasingly large number of electronics manufacturing applications in recent years. Nevertheless, research and testing of no-clean manufacturing processes is ongoing in hopes of making it a viable alternative in a wider variety of uses. Second to no-clean with respect to ozone layer protection is aqueous or semi-aqueous cleaning. The major drawbacks of these alternatives may be high energy consumption and wastewater treatment costs.

HCFCs, though their use is transitional, are important alternatives to CFC-113 and 1,1,1-trichloroethane solvent use in applications for which no other viable alternative exists. Because of their lower ozone-depletion potential, HCFCs with a short lifetime (below 10 years) are preferred to those with longer lifetimes (over 15 years). However, HCFCs should only be used as substitutes for 1,1,1-trichloroethane if their ODP is lower than 0.10 and if their emissions are controlled using the best available technology. As a result of the 1992 Copenhagen Amendments to the Montreal Protocol, HCFC use is only a temporary alternative. The amendments state that consumption of HCFCs must be reduced by 99.5% by 2020 and completely phased out by 2030. In the interim, the Protocol recommends that HCFCs only be used in conjunction with emission control recovery and recycling systems. Thus, HCFCs are a valid alternative in certain limited applications while other, long-term alternatives are being developed (Yamabe 1991).[4]

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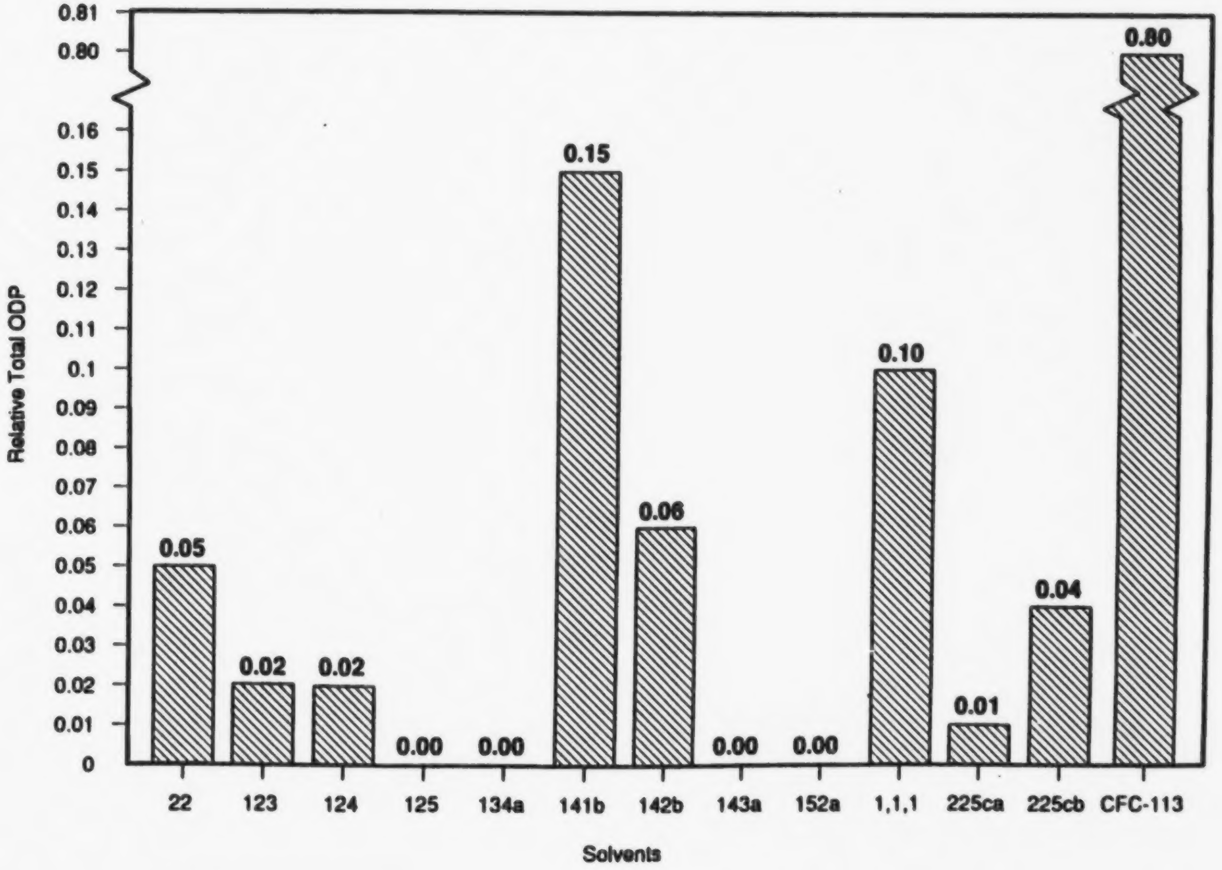
[4] Low ODP alternatives, coupled with recovery systems, could be effective in protecting the ozone layer. The recovery system would be effective in reducing the consumption of ozone-depleting chemicals in small factories, where more than 50 percent of the consumption of these chemicals takes place (Yamabe 1991).

Figure I-2.

RELATIVE TOTAL OZONE DEPLETING POTENTIAL OF SELECTED HALOGENATED SOLVENTS*



* Relative to CFC-11 which is set at a value of 1.

11n077-1

CHAPTER 2

ELECTRONICS INDUSTRY APPLICATIONS

2.1 BACKGROUND

Since the publication of the 1991 Solvents, Coatings and Adhesives Technical Option Committee (TOC) report, considerable practical, commercial, and technical developments have occurred. Several nations, including Germany, Sweden and Switzerland, already have legislation in force to phaseout ozone-depleting solvents. Many other countries, as well as individual users, have achieved spectacular reductions.

Unfortunately, some electronics companies in some nations are unprepared for the 1 January 1996 phaseout. This situation is difficult to understand, as the electronics industry has found reasonable solutions for practically all the problems that have arisen.

This chapter has been rewritten, not merely updated, in an attempt to keep it a manageable size and due to the significant progress that has occurred in the electronics industry.

The principal use of CFC-113 and 1,1,1-trichloroethane (methyl chloroform) solvents in the electronics industry is for defluxing, that is, the removal of residues from assemblies after soldering. The flux or solder paste residues[1] are characterised as a mixture of:

- raw flux
- thermally modified flux
- flux decomposition products
- reaction products between the flux components and metal oxides from the printed circuit boards, the component leads, and the molten solder
- residues - modified or otherwise - from contaminants previously left on the boards and components
- residues from soldering oils
- paste modifiers.

A further use for 1,1,1-trichloroethane is in printed circuit fabrication as a developer for photosensitive coatings, mainly dry film photoresists and dry film solder masks.

The dissemination of information to small production units on substitutes for ozone-depleting solvents is a problem in many nations. This may be due to difficulty in assessing substitutes and because companies are often too small or too remotely located to use consultants effectively.

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[1] In this chapter, the word flux may be considered as including solder paste, except where there is a significant distinction specified.

Language may also play a significant role, as most of the information is published in English. This has been discussed in the 1994 TEAP report (UNEP 1994).

One other factor which has retarded the phase-out of CFC-113 in the electronics industry has been specifications which discouraged using substitute cleaning processes for military and similar applications. Much ordinary electronics production, particularly in the smaller firms, was cleaned to military approved requirements using CFC-113 and 1,1,1-trichloroethane, even though it was not strictly necessary. To avoid duplication of processes and equipment, the military standards were used for non-military work, which resulted in unnecessarily large CFC emissions. In February 1991, the U.S. military adopted MIL-STD-2000,[2] Revision A (DoD, 1991). This standard conditionally permits the use of non-rosin fluxes and non-ozone depleting solvents and cleaning processes for most electronics assembly and retroactively for existing contracts. MIL-STD-2000 (Rev A) also recommends that CFC solvents "be phased out". This revision to US military standards has already had a far-reaching and global effect. Nevertheless, there is little room for complacency, as was shown by the report to a recent conference concentrating on these problems (NATO 1994).

In the electronics industry, there are six primary methods that are suitable for replacing ozone-depleting substances (ODSs) (Figure II-1), each with a number of important variants. The following list, although not exhaustive, is a general review of these as they apply to fluxes and solder pastes.

- "No-Clean" methods, including controlled atmosphere soldering
- Water soluble fluxes and water cleaning
- Rosin fluxes + saponifier + water cleaning
- Rosin & SA fluxes + hydrocarbon/surfactant + water cleaning
- Rosin & SA fluxes + hydrocarbon and derivative (including alcohol) solvent cleaning
- Rosin & SA fluxes + permitted halocarbon solvent cleaning.

Due to the numerous financial and environmental considerations, the Solvents TOC recommends that the substitute process be fully tested, qualified, and found satisfactory *under full production conditions* before any capital investment is made. In addition, the process and its supporting infrastructure should include approval by all the appropriate fire, health, safety, and environmental authorities.

The following list of questions can help users decide whether or not to clean:

- is human life at stake?*
- is the assembly working at high frequency or high impedance?*
- are analogue signal levels low?*

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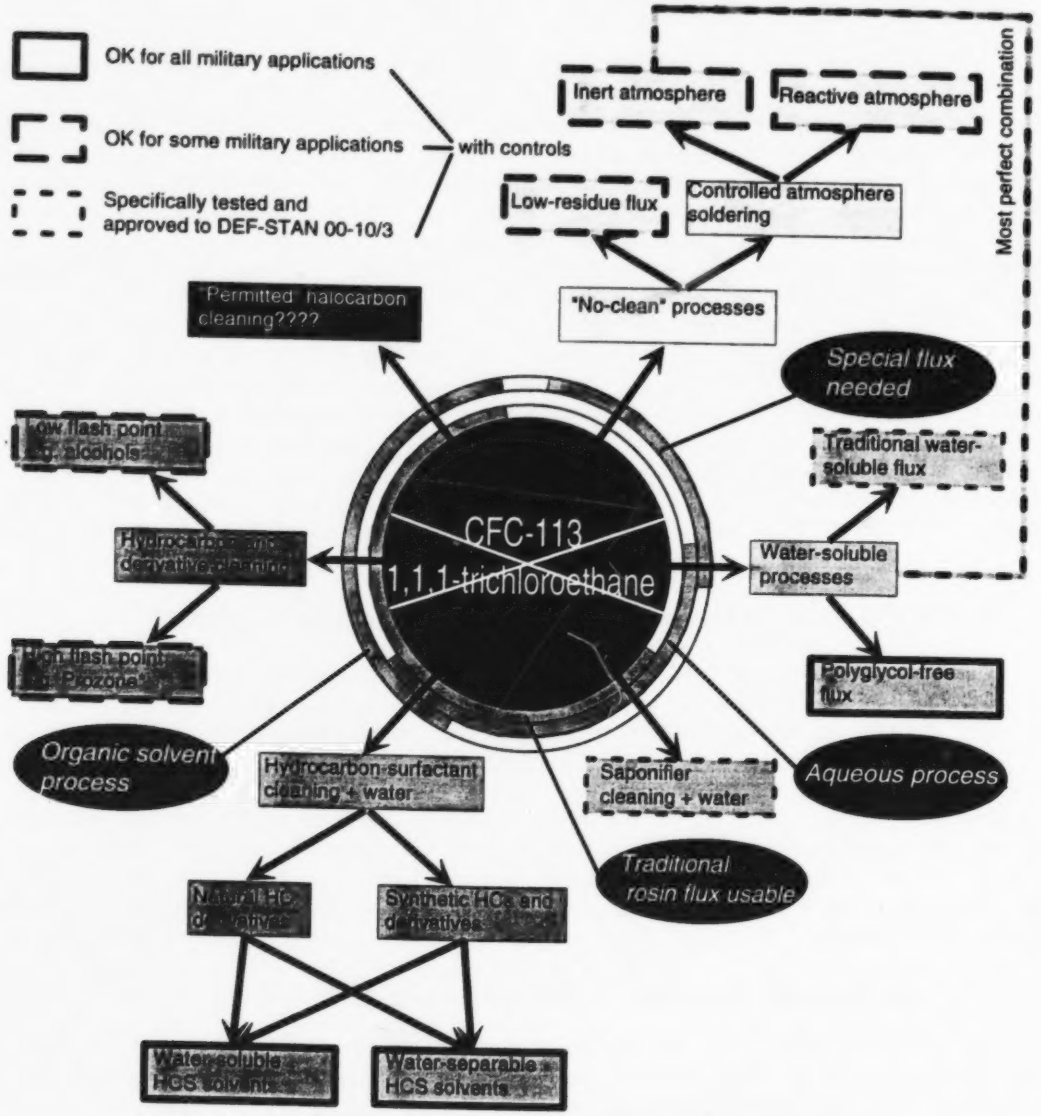
[2] This standard details requirements for the materials and processes which may be used in making soldered connections in electronic assemblies. The soldered connections which must meet this standard's specifications include: lead and wires inserted in holes, surface-mounted components, and components attached to terminals.

Replacement of OD solvents in the military electronics industry


OK for all military applications
OK for some military applications
Specifically tested and approved to DEF-STAN 00-10/3
with controls
Inert atmosphere
Reactive atmosphere
Most perfect combination
Low-residue flux
Controlled atmosphere soldering
"Permitted" halocarbon cleaning????
"No-clean" processes
Special flux needed
Low flash point e.g. alcohols
Traditional water-soluble flux
Hydrocarbon and derivative cleaning
CFC-113
1,1,1-trichloroethane
Water-soluble processes
High flash point e.g. Prozone*
Polyglycol-free flux
Organic solvent process
Hydrocarbon-surfactant cleaning + water
Saponifier cleaning + water
Aqueous process
Traditional rosin flux usable
Natural HCs derivatives
Synthetic HCs and derivatives
Water-soluble HCS solvents
Water-separable HCS solvents

* Prozone is a registered Trade Mark of British Petroleum Chemicals Limited.

Figure II-1. Methods of replacing ozone-depleting solvents in the electronics industry.

- is reliability important?*
- are assemblies likely to be subject to high temperatures[3], high humidity or rapidly changing atmospheric conditions?*
- are assemblies to be conformally coated?*
- does the customer specify high reliability standards?*
- does the customer exact a long guaranteed lifetime?*
- is cost subordinate to other factors?
- is the aspect of the circuit important?
- is automatic testing to be done?
- is burn-in of the finished assembly done?

The questions with an asterisk (*) are more important in the decision process.

Where cleaning is necessary, there are problems of scale. With CFC-113 vapour defluxing, the equipment price is roughly proportional to the throughput capacity; this, however, is not always the case with substitute methods. To achieve a change which produces a satisfactory quality, small manufacturers in both developing and developed nations may have to pay disproportionately more for the equipment. In many instances, these capital costs may be offset by lower operating costs.

Finally, before assembly is done, the design of the printed circuit is an all-important factor which is frequently ignored. Successful use of "No-Clean" fluxes, particularly with wave-soldered SM components, is dependent on correct PCB design. Similarly, if cleaning is to be carried out, the criteria are very different and other design factors are required. Often a circuit which gives excellent results with one process gives very poor results with another. Section (2.2) is a new section which addresses this problem.

2.2 PRINTED CIRCUIT DESIGN FOR EFFICIENT SOLDERING AND CLEANING

The use of certain soldering and cleaning processes can be optimised only if the PCB is designed correctly *for that process* (Ellis 1994). The use of anything other-than-optimised may seriously compromise the efficiency of the chosen process. This section gives the designer an introduction to the subject. A designer must be informed as to which soldering and cleaning processes are to be used in production before starting work. It is assumed that the designer uses a quality electronics CAD system, without it being specific to one type. Users of manual draughting, low-cost CAD systems or those adapted from mechanical CAD packages may have to make some modifications and make many manual retouches to comply with the following recommendations.

2.2.1 Low-Solids "No-Clean" flux wave soldering

The use of Low-Solids "No-Clean" fluxes presents the biggest challenge to the PCB designer, particularly for the SMD circuit. The PCB design is critical to exploit the operating window, which can be quite small.

Traditional High-Residue fluxes for SMD soldering present a severe disadvantage when soldering SMD components with a conventional wave soldering machine. The components themselves create "shadows" which prevent correct soldering from taking place. This was circumvented by using "double-wave" soldering machines: the first wave was very turbulent to ensure the solder penetrated into the "shadows", but left uncontrolled amounts of solder on the joints and between conductors. The second wave was a smooth, streamline wave whose function was to remove the excess solder and to leave sufficient to form a perfect meniscus at each joint.

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[3] Rosin fluxes start to soften at about 70°C.

Without extensive engineering it is generally not possible to use the "double-wave" technique with Low-Solids "No-Clean" fluxes because the turbulent wave offers sufficient agitation so that the quasi-totality of the flux activator is removed. The second wave has to operate practically without activator present and the solder joint which results is usually defective. A few Low-Solids "No-Clean" fluxes are designed to permit double-wave soldering but these may present other disadvantages. It is therefore necessary to ensure, by careful layout, minimum shadowing by the components, so that a single wave may be used.

Design for Low-Solids "No-Clean" flux soldering of SMD circuits implies that no solder joint be placed on the last side of the component to "see" the solder wave. With components that have connections along two sides, such as passive chip components and SMSO ICs, these should present themselves so that all the solder lands be on either side of the device as "seen" by the wave. A problem obviously presents itself with components which have soldering lands along all four sides, such as gull-wing, J-lead PLCCs, or LCCCs. Shadowing may be minimised by placing this type of device at 45 degrees to the wave angle. This generally works with the better fluxes. Some of the less versatile CAD systems do not permit turning components through 45 degrees or, if they do, they may not allow the connecting tracks to come out in a very logical way. This would imply that the component actually be designed specifically in the library at the required angle, thereby using up four custom pad (land) sizes, instead of one. The best method uses a rectangular pad design with the actual connection offset to the outer edge, if the design rules do not allow the connection to be forced at the designed angle. Some manual retouching may be needed after autorouting. As cleaning will not be carried out, the pad width may be as wide as is necessary to ensure that bridging does not occur and that the minimum gap width be respected. Via holes should be spaced away from the pad by an intermediate connection between them and the hole of a minimum of 1 mm, even if they are tented, filled or otherwise rendered unsolderable. The major axis of the interconnecting tracks should be parallel to the axis of the soldering machine, even if they are covered with a solder resist or mask, in order to ensure minimum solder balling. For double-sided boards with wave-soldered SM components on both sides, this implies that the boards be soldered in different directions for each side, as most CAD systems force the major routing at 90 degrees; in any case, this uses the "real estate" most efficiently. With multilayer circuits, the problem is not the same as both the outer layers may be forced in the same direction, according to the flexibility of the design rules of the system.

Figure II-2 illustrates an example of a hypothetical design for Low-Solids "No-Clean" soldering.

2.2.2 Controlled Atmosphere Soldering

This presents exactly similar problems to that of the Low-Solids "No-Clean" flux case and the same criteria apply, as in the preceding section.

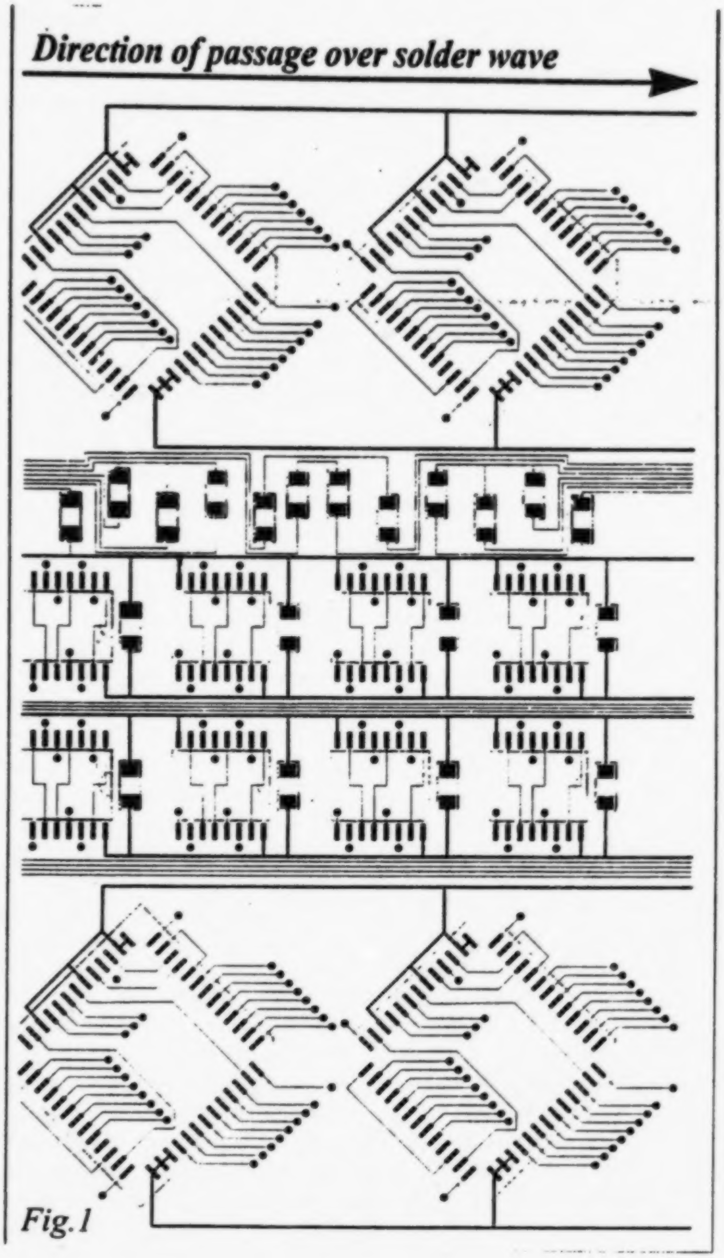

Direction of passage over solder wave
Fig.1

Figure II-2. Hypothetical example of SMD circuit designed for "No-Clean" wave soldering showing correct orientation of components.

2.2.3 "Traditional" flux soldering and cleaning

"Traditional" fluxes may be considered as activated rosin (RMA, RA or F-SW32 halide free) or water soluble types. The design criteria for soldering with these fluxes are far less critical and therefore the accent is best placed on cleaning. For through-hole circuitry, no change is required to the design rules. The problems arise when cleaning SMDs.

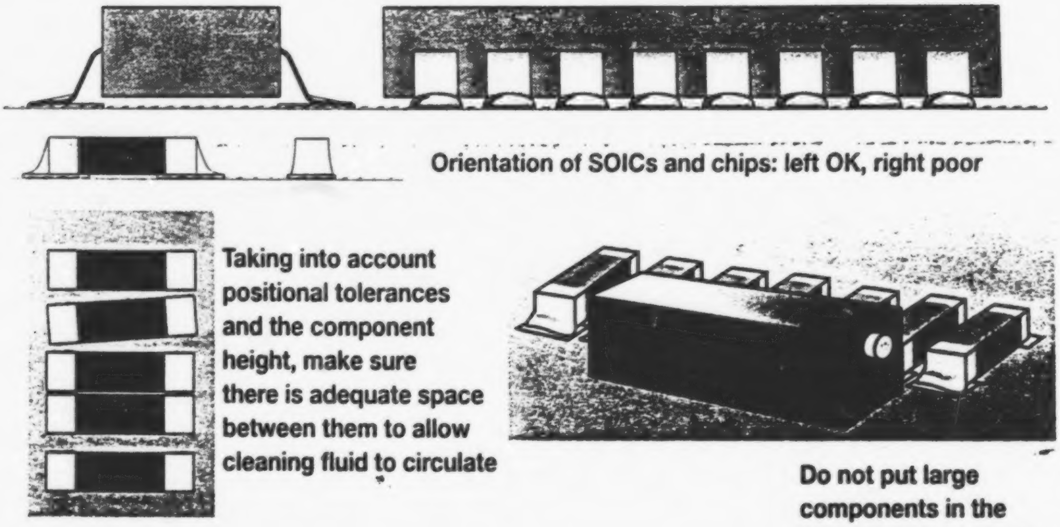
In reality, cleaning with CFC-113 is, in most cases, just as difficult as with any of the substitute processes, if not more so. This section therefore applies to all cleaning methods.

The cleaning solvent, be it aqueous or organic, must penetrate as freely as possible under the components and, having penetrated, must circulate. Young's law indicates that pure water, with a high surface tension, will penetrate better, by capillary action, into close spaces than would an organic solvent or a less pure water, with a lower surface tension. If free circulation is to take place, then the spaces must be as wide as possible and the obstructions be minimised. It is therefore important to choose those components which have the largest stand-off from the printed circuit board. With plastic moulded components, it is quite usual to place small stand-off "blips" in the corners. Ideally, these "blips" should also have the smallest surface area, although this criterion is secondary to the height. Smaller components, such as 1206 passive chips, have relatively little difficulty, as far as cleaning is concerned, because of the small area to stand-off ratio.

The placement of wave-soldered SM circuits is therefore the most critical factor and should, as ideally as possible, be done as a function of the component height. Some CAD systems will permit autoplacement where component height can be a function by limiting tall components to specific parts of the boards, while retaining coupled components (e.g. decoupling capacitors). The space round tall components should also be greater than round low ones. This can be done by using a larger rectangular silk profile than that of the component itself and replacing it after the layout is completed by an autolibrary function, if there is no other way possible to ensure the best conditions within the framework of the CAD system. When considering component spacing, it must be assumed that worst-case positional tolerancing will occur: it is therefore a mistake to force components too closely together: in fact, the ideal situation is to use the "real estate" of the PCB to best advantage to maximise component spacing. Orientation is also critical. This should be arranged to allow the maximum ingress of cleaning fluid, so the design is also a function of the way the finished circuit will pass through the cleaning machine and of the way that the machine operates. In-line conveyorised spray machines with the jets normal to the surface of the board are generally less efficient than batch machines where the jets may attack the boards at an angle as small as 15 degrees. On the other hand, the former are perhaps much less prone to shadowing problems as the liquid can penetrate the inter-component space more readily, even if it tends to "puddle" and stagnate there, rather than circulate.

Figures II-3 and II-4 show a few ideas as to the best principles to adopt when designing the placement of boards to be cleaned. Pad width becomes very critical, in this case, as having a broad solder meniscus on four-sided connection components will reduce the ingress of cleaning fluids by as much as 50 percent, especially if the solvent loses kinetic energy by striking the

Layout criteria for effective cleaning



Orientation of SOICs and chips: left OK, right poor

Taking into account positional tolerances and the component height, make sure there is adequate space between them to allow cleaning fluid to circulate

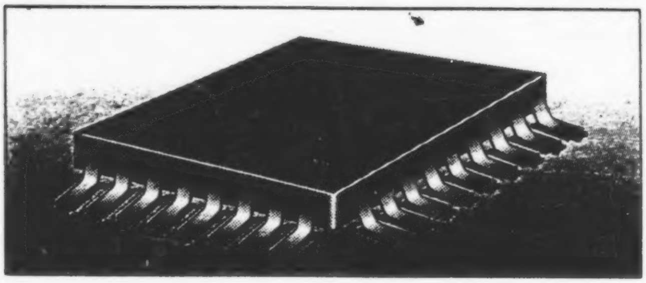
Do not put large components in the line of spray to smaller ones

Fig.2

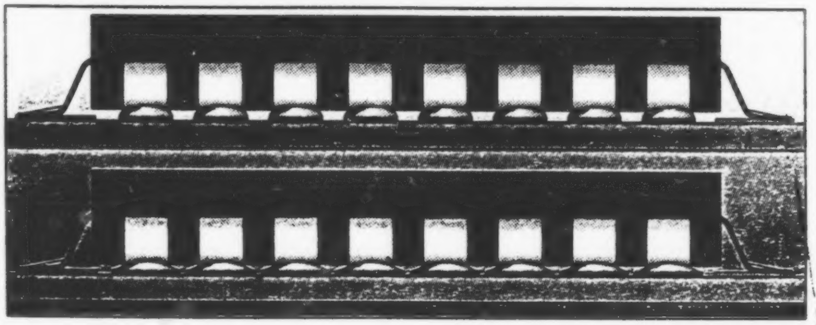
Figure II-3. Layout criteria for effective cleaning a) orientation and position

Layout criteria for effective cleaning

Components placed at an angle: Solder joints brake the energetic ingress of cleaning products.



Minimal sized soldering lands: maximum ingress of cleaning products.



Solder lands too wide: ingress of cleaning products reduced by 50%.

Fig.3

Figure II-4. Layout Criteria for Effective Cleaning
b) Maximum ingress of cleaning fluids

board surface before being deviated under the components. It is therefore important, in all cases, to use a pad width which is as narrow as possible, but consistent with good soldering quality. Such components must *never* be placed at 45 degrees to the axis of the cleaning machine, as the angle will reduce the "window" between solder joints by 30%: the component must always be axial.

2.2.4 "Glue-spots" and cleaning quality

The position of the Glue-spots on boards which are not cleaned is not very critical, within normal parameters. On the other hand, they may be critical for boards which must be cleaned, as they can restrict the flow of cleaning fluids. With small components, the Glue-spot is generally placed centrally. With heavier components, two or more Glue-spots may be required. If two are used, then the ideal configuration is they should form an axis which is not in line with the cleaning machine (as well as being of minimum size). Either 45 or 90 degrees is generally satisfactory. With three or more spots, care should be taken to avoid shadowing of the space between them. Most good CAD systems can automatically incorporate the Glue-spot positions in the component libraries, according to the operator's wishes.

2.2.5 "No-Clean" Paste Reflow soldering

Most "No-Clean" pastes have considerably higher residue levels than many other "No-Clean" soldering processes as the chemistry must contain sufficient product to ensure the correct viscosity and rheological characteristics. As the paste is reflowed homogeneously by infra-red radiation or by vapour phase PFC heating, there are few orientational problems. As such, there are few critical design parameters other than those imposed by the soldering process itself. Soldering land width and spacing may be critical and the CAD design rules may need some fine tuning. During component placement, the distance between components must be sufficient to permit the heating medium to pass. One of the main difficulties which is sometimes encountered is that of solder balls. These may cause electrical and/or mechanical problems but they are not so much a design problem as one of the soldering conditions themselves and the paste quality and age. Even more important than with wave soldering, via holes must be well separated from the soldering pads or lands, otherwise the molten solder may be drained from where it is necessary.

2.2.6 "Traditional" Paste Reflow Soldering and cleaning

The design rules for rosin or water-soluble paste are similar to those for "No-Clean" pastes. The components should be selected with maximum stand-off heights and with other characteristics suitable for reflow and wave soldering.

2.3 CFC-113 USE IN ELECTRONICS ASSEMBLIES

2.3.1 Major Assembly Processes

Electronic components are fluxed and soldered to electronic assemblies and then cleaned to remove flux residue and other contaminants introduced in the production process. The electronic components are attached by either through-hole assembly technology or by surface-mounted assembly technology or a combination of the two. The actual techniques are only secondary to the problems of cleaning, so they will not be discussed here. For further details, please consult the 1989 and 1991 Solvents TOC reports (UNEP 1989, 1991) or other literature (Ellis 1986).

Boards are soldered in one of two general ways: (1) a molten solder is used to solder and secure the components onto the board or (2) a solid solder (normally in the form of wire solder or small solder spheres in a flux paste matrix) is deposited on the board and later heated. Wave, dip, and drag soldering are examples of the former; manual, infra-red, condensation reflow, or hot gas soldering are examples of the latter. Wave soldering is commonly used in high-throughput electronic assembly operations. Wave-soldered boards are fluxed and passed over a wave of solder that flows up from the solder bath. The solder forms an intermetallic bond with the surfaces of the component leads and tracks and with the plated through-holes of the printed wiring boards.

Flux is removed from electronics assemblies to:

- remove corrosive flux ingredients
- improve adhesion of conformal coatings
- enable easier visual inspection
- facilitate automatic testing
- minimise leakage currents
- enhance product appearance
- to conform to customer specifications

The need for post-solder flux-residue cleaning varies widely and depends on the final electronics application. For example, most printed circuit boards that are used in toys and home appliances are cleaned perfunctorily, if at all. In contrast, boards that are manufactured for automotive, military, space, medical and other critical applications require high levels of cleanliness. Frequently, boards require cleaning for automatic testing rather than for reliability (IPC 1986). However, in applications where assemblies are exposed to elevated temperature and humidity, flux residues can corrode metallic tracks on electronics assemblies and component leads and also create deleterious effects on the electrical characteristics of the insulation (see Section 2.1).

2.3.2 Flux Types

"No-Clean", rosin/resin, synthetically activated, and water-soluble (also frequently referred to as organic acid) are the major flux types.

There are several variations in so-called "No-Clean" flux types, containing quantities of resins (some with wood rosin) ranging from zero up to about 5% w/w. They all have high degrees of activation, compared to more traditional rosin or resin fluxes. In extreme cases, the solid matter may be entirely activators. The activators are most frequently based on non-halogenated linear carboxylic acids, although some types also use cyclic acids or organic hydrohalide compounds either alone or in combination. They are also referred to as "Low-Solids" fluxes. The terminology, in either case, is not necessarily precise as some fluxes with a low solids content may possibly lend themselves to cleaning and some fluxes with a higher solids content may be perfectly adapted to not being cleaned (DIN-Normen). As a general rule, the operating "window" when soldering with "No-Clean" fluxes is narrower than with many other flux types and they are often more prone to cause solder-balling (solder balls are small metallic spheroid particles of typical diameters within the range of 0.05 to 0.5 mm and which tend to adhere to the printed circuit substrate.)

When properly prepared, traditional rosin fluxes meet U.S. military specifications (MIL-F-14256),[4] have a history of successful use, and do not always need to be removed after soldering. Rosin is a complex mixture of isomeric acids and rosin fluxes are classified by the amount of activator present. Activators, generally halides or carboxylic acids or a combination of both, increase the wetting ability of the solder by reducing oxides present on the surfaces to be soldered. While they are the least corrosive and conductive fluxes, rosin fluxes have limited wetting abilities.

The small amounts of post-soldering board residue can minimise cleaning problems or eliminate the need for cleaning. Toubin (1989) found that Low-Solids fluxes can be both efficient and cost effective when run under tight process control. A later report (Toubin 1991) has indicated that many of these fluxes may cause corrosion, and SIR problems. These and other problems have been corroborated by a small number of users who have reverted to cleaning after many months of using "No-Clean" techniques for medium-reliability applications.

Synthetic activated (SA) fluxes (more active than rosin fluxes, but less active than many water-soluble fluxes) were initially designed to be removed specifically with CFC-113. Compared to rosin fluxes, synthetic activated fluxes, because of their activity, improve the wetting by the solder. SA flux residues must be removed immediately after soldering. SA fluxes have never held more than a small share of the market and, since the reduction of use of CFC-113 and 1,1,1-trichloroethane solvents, this share has been reduced even further. This loss of market share is because SA flux has little specific advantage except when used with ozone-depleting solvents.

There are a variety of formulations for water-soluble fluxes which usually contain relatively large percentages of activators (compared with rosin fluxes), such as organic acids, hydrochlorides, hydrobromides and amines dissolved in water or, more usually, alcohol solvents. Water-soluble fluxes, in general, allow faster soldering rates with fewer rejected boards due to solder defects and do not require a saponifier when cleaned with aqueous cleaning systems. Water-soluble fluxes, as currently formulated, are usually more corrosive than other fluxes. Subsequent board and component damage can only be prevented by thorough and immediate controlled cleaning. It may be necessary not only to use purified water in aqueous cleaning processes, but also to treat waste water.

Although aqueous cleaning is used in a number of electronics industry applications, it is not approved for all applications. In the past, U.S. military electronic assembly specifications did not allow water-soluble fluxes, but such flux types were acceptable for British military applications (DEF-STAN 00/10-3, Baxter 1989). The latest revision to the U.S. military Tri-Services soldering and assembly standard, MIL-STD-2000,[5] Revision A (issued 14 February 1991), however, allows the use of non-rosin fluxes provided specific test and quality criteria are met. Some specialised boards contain materials, such as polyimides and certain glazes in hybrid circuits, that are incompatible with aqueous cleaning that employs saponifiers. Also, some water-soluble fluxes with certain polyglycol derivative constituents may be deleterious to the resin substrate of printed circuit boards particularly where the base material is of poor quality or has been incorrectly polymerised. In this case, cleaning leaves a porous surface with flux residues absorbed into the surface of the printed circuit board. These hygroscopic residues may cause surface insulation resistance problems under conditions of elevated temperature and humidity. The majority of water-soluble fluxes do not cause this problem, but it is advisable to conduct tests before adopting fluxes of this type. This problem of surface attack is independent of the more common, relatively benign, lowering of surface insulation resistance due to adsorption of micellar substances on substrate surfaces. This latter phenomenon is frequently temporary and is reported not to degrade performance or long-term reliability (Fisher 1991). Inorganic fluxes are too corrosive for electronics soldering in most instances (Ellis 1989). Table II-1 lists common circuit board assembly contaminants.

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[4] This specification consists of a list of fluxes, rosin-based liquids, and pastes which have been approved for military use. Specifically, they are intended for use in the assembly of electronic circuitry and electrical equipment using tin-lead solders.

Once a flux has been qualified, users should cooperate with vendors to ensure consistent quality. This is particularly important where natural products are used in the formulation of the flux.

2.4 PRODUCTION PROCESSES

Referring to Figure II-1, a brief commentary and the advantages and disadvantages of each of the basic process will be discussed.

In all the following cases, no differentiation is made between wave soldering using some form of liquid flux, hand soldering using flux-cored wire or reflow soldering using solder pastes, except where specifically mentioned.

2.4.1 "No-Clean" processes

Many "No-Clean" processes are difficult to understand, but they can provide reliable, economical, and high quality production. These processes often provide the first choice for CFC-113 replacement, where the quality is acceptable for the application. Because there is no post-soldering cleaning, any contaminants present on the components or PCB before fluxing may cause a greater loss of reliability of the finished assembly than the "No-Clean" flux residues themselves.

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[5] This standard details requirements for the materials and processes which may be used in making soldered connections in electronic assemblies. The soldered connections which must meet this standard's specifications include: lead and wires inserted in holes, surface-mounted components, and components attached to terminals.

Table II-1. TYPICAL CIRCUIT BOARD ASSEMBLY CONTAMINANTS[a]

Category 1*	Category 2	Category 3
Resin and Fibreglass Debris from Drilling and/or Punching Operations	Flux Activators	Flux Resin
Metal and Plastic Chips from Machining and/or Trimming Operations	Activator Residues	Flux Rosin
Dust	Soldering Salts	Oils
Handling Soils	Handling Soils (Sodium and Potassium Chlorides)	Grease
Lint	Residual Plating Salts	Waxes
Insulation	Neutralisers	Synthetic Polymers
Hair/Skin	Ethanolamines	Soldering Oils
	Surfactants (ionic)	Metal Oxides
		Handling Soils
		Polyglycol Degradation Byproduct
		Hand Creams
		Lubricants
		Silicones
		Surfactants (non-ionic)

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[a] Contaminants may exhibit characteristics of more than one category.

*

Category 1 -Particulate
Category 2 -- Polar, ionic, or inorganic
Category 3 -- Nonpolar, non-ionic, or organic
Source: ANSI/IPC-SC-60 1987.

2.4.1.1 Low-Solids "No-Clean" processes

These processes use fluxes which may operate according to a number of different principles. The original types were simply variants of traditional fluxes of the DIN 8511 F-SW32 (halide-free rosin), which were diluted to typically one-half to one-third the solids content. The ratio of activator to rosin was generally much higher. These early fluxes were difficult-to-use. These were followed by a number of fluxes with greatly reduced rosin or synthetic resin content and an even higher activator content. These ones had a slightly wider operating window. Typical activators were adipic and succinic acids which were fairly stable at soldering temperatures. The next generation used flux systems which sublimated at soldering temperatures. This allowed higher solids content to be used for a reduced volume of residues, making for considerably easier soldering.

Advantages:

- Economical soldering
- No cleaning machine or space required
- Environmentally easy to control
- Residues may be cosmetically acceptable

Disadvantages:

- Restricted operating window
- Reliability of assembly needs to be determined
- Higher-than-average retouch rate
- Some types not suitable for conformal coating
- Many types unsuitable for high-reliability applications
- Solder-balling may be a problem (not with hand-soldering)
- Cleaning not possible with many types
- Double-wave soldering very difficult
- Residues may cause corrosion
- Residues may deteriorate electrical characteristics

2.4.1.2 High-solids "No-Clean" processes

These use traditional rosin-based fluxes to R, RMA or RA specifications or to DIN 8511 F-SW32 standards.

Advantages:

- Economical soldering
- No cleaning machine or space required
- Environmentally easy to control
- Easy soldering
- Cleaning usually possible, if necessary

Disadvantages:

- Reliability of assembly needs to be determined
- Generally unsuitable for conformal coating
- Many types unsuitable for high-reliability applications
- Automatic testing usually not possible
- Residues unsightly and frequently sticky
- Pastes may tend to solder ball

- Residues may cause corrosion
- Residues may deteriorate electrical characteristics

2.4.1.3 Controlled atmosphere soldering

Controlled atmosphere soldering can be divided into two types: reducing and inert atmosphere. Technically, reducing atmospheres are difficult to maintain and operate at ordinary soldering temperatures but may reduce the needs of fluxes to extremely small levels, leaving very little flux-related contamination[6]. Inert-atmosphere soldering is usually done under pure nitrogen with strictly-controlled oxygen levels. Inert atmosphere wave soldering uses a flux which is sometimes called a preparation fluid. Early types were based on a simple dilute adipic acid solution in isopropanol. The latest generation sublime on the solder wave so that the small quantity of flux almost completely vaporise: the relatively high vapour content may recondense in a polymerised form on the cooling circuit as the PCB leaves the machine. This leaves a microscopically thin protective coating. Solder pastes for controlled atmosphere reflow must be formulated to have the right ratio for the correct rheological characteristics. This makes them leave residues which are more visible than with wave soldering.

Advantages:

- Little dross formation on solder waves
- Lowest "No-Clean" residues
- Environmentally easy to control
- Residues may be cosmetically acceptable
- If required, aqueous cleaning is usually easy
- Minimum heavy metal salt formation

Disadvantages:

- Restricted operating window
- Reliability of assembly needs to be determined
- Higher-than-average retouch rate
- Of doubtful value for conformal coating
- Many types unsuitable for high-reliability applications
- Solder-balling may be a problem
- Residues may cause corrosion
- Residues may deteriorate electrical characteristics
- High capital costs
- High costs of nitrogen

2.4.2 Water soluble processes

The use of water soluble fluxes and pastes represent the most economical manner of soldering and cleaning. Many major users have been using them continuously since the early 1960s. Up to recently, most of the fluxes used at least some organic hydrochlorides as activators, with some form of glycol derivative as a vehicle. For about fifteen years, it has been known that a few of the glycol compounds have caused a deleterious effect on the insulating characteristics of some organic substrates. This effect has been studied but little major work was done to characterise the phenomena and to avoid it. Recently, a number of glycol-free products have appeared on the market, frequently also halide and VOC-free (or nearly so)[7]. These have generally shown themselves to be somewhat more difficult to use, but may be useful where a maximum Surface Insulation Resistance (SIR) is essential.

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[6] It has been stated on a few occasions that it is possible to solder in an inert atmosphere without any flux, at all. This may be theoretically true under ideal conditions: in practice, some way of reducing oxides on component leads and the PCBs must be present.

The aqueous method has proved to be highly popular where the conversion away from a CFC-113 process has already been made and a cleaning operation has been deemed essential.

As with all processes, these do require careful quality management. Less-than-perfect cleaning may produce catastrophic results. Post-soldering cleaning may be done with just a simple water wash followed by a succession of water rinses. For best results, at the price of a slightly higher manufacturing cost, the final rinses may be achieved with deionised water, particularly for high-reliability work or where the tap water quality is poor. Better results may be obtained by using a chelating solution for the first wash, to ensure perfect solubilisation of the heavy-metal salts resulting from the soldering process, again indicated for high-reliability processes. Several advantages can also result from the addition of a few percent of isopropanol to the last rinse water (Protonique 1993).

2.4.2.1 Traditional water soluble process

This process consists of soldering with the help of a water soluble flux using organic hydrohalide activators, containing little or no water in the solvent base. The high flux activity makes this process easy-to-master with extremely low retouch rates. The cleaning process is easy and the overall results are suitable for most applications.

One problem common to all pure water processes is that of retouches and hand soldering. Water soluble flux cored solder wire of all types is available from many manufacturers, but are not popular because of the fumes they produce. Good air extraction from the soldering zone is highly recommended, so that the same cleaning process may be used for mass-soldered and for retouched boards.

Advantages

- Lowest cost of all soldering/cleaning processes
- Easy soldering
- Low retouch rate
- Very good residual cleanliness, even under SMDs
- Water treatment easy and cheap
- Wide range of machines available
- 30 years of track record

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[7] All organic fluxes of all families contain volatile organic compounds (VOCs). Although the solvent system is usually quoted as the main source of VOCs, the activators, surfactants and vehicles also are the sources of emissions of VOCs at soldering temperatures.

Disadvantages

- Good cleaning quality essential - no half measures
- Possibility of slightly poorer SIR
- Users are afraid to try it

2.4.2.2 "Glycol-free" water soluble process

This relatively new substitute process has raised some interest in military circles. The prototype fluxes of this type were developed about twenty years ago. One German manufacturer marketed a flux using citric acid as activator, a triol as vehicle, a small amount of a non-ionic surfactant and alcohol, with a small quantity of added water, as a solvent. Over fifteen years later, an American company developed a flux consisting of citric acid, a small amount of non-ionic surfactant and water. This latter development dispensed with the triol and the alcohol to reduce the VOC content, an added advantage in regions with rigorous VOC legislation, but at the cost of narrowing the soldering "window". Another multinational flux manufacturer announced in 1989 another type of polyglycol-free flux in both low VOC and "normal" versions, employing completely different vehicle and activator chemistries. Some of the fluxes in this range may be employed as "No-Clean" products or for water cleaning, according to the individual circuits being soldered.

Advantages

- Low cost soldering/cleaning processes
- Very good residual cleanliness, even under SMDs
- Water treatment easy and cheap
- Wide range of machines available
- No SIR deterioration
- Some products low VOC

Disadvantages

- Good cleaning quality essential - no half measures
- Some potential users "afraid" of trying it
- Reduced operating "window" of soldering operation

2.4.3 Saponification processes

Saponification is a chemical reaction which modifies insoluble rosin into a water-soluble rosin soap which can then be removed in a similar washing process (2.4.2) as used for water soluble processes. As it is a chemical process, it is necessary to use reactive products, generally highly alkaline mixtures based on monoethanolamine. These aggressive products require careful handling. For this reason, this process has not been as popular as the excellent results may suggest. Cleaning quality has been shown to be outstanding (Grossmann 1993), but this process works best with thin residue layers. Although slightly more expensive than water soluble flux processes, the overall cost is acceptable.

Advantages

- Reasonably low cost soldering/cleaning processes
- Very good residual cleanliness, even under SMDs
- Water treatment reasonably easy and cheap
- Wide range of machines available
- No need to change flux type in many cases
- Over 25 years of good track record

Disadvantages

- Good cleaning quality essential - no half measures
- Users are reluctant to try it
- Health and Safety concerns
- Thick rosin residues may require long cycle times
- Potential incompatibilities with amphoteric metals and polyimide substrates
- Selection of most suitable saponifier may require much work

2.4.4 Hydrocarbon-Surfactant (HCS or HC/S) Processes.

Also - incorrectly - known as "semi-aqueous" processes, HCS methods have not seen the commercial success originally forecast. This is due to high drag-out losses, up to 4 $g.dm^{-2}$ with densely populated SMD circuits (Scolari 1993), high equipment cost, VOC concerns, combustibility, difficult recovery and water treatment etc. Nonetheless, there remain many niche applications where HCS processes may be suitable and economical.

The basic principle is simple and effective. Rosin flux based soldering residues are solubilised in an organic solvent whose vapour pressure is fairly low. The contaminated solvent is then removed by a full water wash, usually very similar as is required for cleaning off water soluble fluxes (2.4.2). This immediately shows that the cleaning equipment must therefore be designed with both the solvent and aqueous phases in mind. Chemically, the solvents may either be natural derivatives, such as terpene-based substances, or synthetic hydrocarbons and derivatives. There is no specific advantage in using the natural products - even though some may be derived from citrus fruits, for example - from the points of view of health, safety and the environment. In fact, many (but not all) synthetic products are considerably less toxic than those made from citrus fruits.

There are two basic methods used in HCS processes and the equipment for each is completely or partially incompatible with the other. These can be considered as "separable" and "miscible" types. Separable types are based on light hydrocarbon derivatives with a specific gravity of less than about 0.9 and which do not mix with water. In order to solubilise it in water, it is blended with a surfactant which allows an unstable emulsion to form. The water emulsion, if allowed to remain still, will separate out so that the solvent will float on the surface of the water/surfactant mixture. It can thus be easily recovered for a partial recycling, but the composition of the separated product is different from the original solvent. Retaining a steady process may therefore be problematic.

The miscible HCS solvents may be subdivided into those which are blended with hydrocarbon solvents and more stable surfactants, producing a permanent emulsion, and those which are hydrocarbons or derivatives which have, within themselves, a surfactant property, often forming a non-micellar solution.

The cleaning part of the process is the same with both categories of HCS products. The main difference is with the waste water treatment and recycling processes.

The cleaning quality of both types of process may be very good, but tests have shown that both water soluble flux and saponification processes are even better (Grossmann 1993). It may be possible that the miscible types are marginally better, although the difference would likely be small.

With separable processes, the initial waste water treatment and/or recycling is done by the separation. The water then has to be treated to remove the surfactant, the heavy metal salts and residual solvents. This is done initially with membrane separation (different membranes may be required for each solvent type), followed by active carbon and deionising resin polishing. The water quality is high enough for recycling up to about 80% of the total water requirements, but the process is expensive and it does not include the treatment of the pollutants. The problem is even more difficult with the miscible types, where the pollutants are almost impossible to remove economically from the waste water. A recent development (Treacher 1993) attempts to use evaporative separation, but it is a very energy-intensive method and the recovered solvent has a considerably different composition compared to the virgin material. It should be stated that most miscible solvents produce a waste water with high BOD_5s, which may not always meet water quality standards.

It is possible that some of the less popular types may simply disappear from the market within the next two or three years. Persons considering these processes would be well-advised to ensure that back-up products exist should their original choice be withdrawn from the market (one major manufacturer and one major distributor have both already dropped the commercialisation of such products).

2.4.4.1 Separable HCS processes

Separable HCS processes are possibly easier to manage as an overall system with recycling of the water and the solvent itself. To achieve this separation requires equipment which is very costly to install, run, and maintain. As such, this process is easier to amortise for very large production rates where the equipment is expected to work at near-maximum capacity 24 hours per day and 7 days per week. Smaller installations without integral recycling may also be used, but may present other problems, outlined earlier.

Advantages:

- Good cleaning quality
- Slightly more forgiving of poor cleaning than many other types

Disadvantages:

- Heavy consumption without recycling
- High capital costs with recycling

- High maintenance costs
- Combustible
- Separation may be at temperatures above the flash point
- Health and Safety concerns
- VOC concerns

2.4.4.2 Miscible processes

Other than for industrial cleaning, there is an important niche market for this type of process: field and service cleaning. One multinational soldering product manufacturer offers a cleaning kit consisting of such a solvent packed in a non-aerosol spray bottle with an adjustable nozzle capable of a jet or fine sprays. For low volume industrial cleaning, this type of process may be suitable without water treatment, but only on condition of prior approval of the water authorities. In view of the high quasi-irrecoverable drag-out losses, this process is very costly for high-volume production.

Advantages:

- Good cleaning quality
- Slightly more forgiving of poor cleaning than many other types
- Very adaptable to low-volume cleaning
- Some products practically non-toxic

Disadvantages:

- Heavy consumption without recycling with water pollution
- High capital costs with recycling
- High maintenance costs
- Combustible
- VOC concerns

2.4.5 HC and derivative processes.

Straight HC solvent cleaning use flammable or combustible solvents. The processes can be divided between those using volatile and flammable solvents such as light alcohols, and heavier, combustible, substances. Light alcohols, by themselves, effectively remove rosin residues but many other contaminants, such as heavy metal salts, may not be correctly eliminated. Some proprietary blends of heavier solvents are remarkably effective cleaners when correctly used but their low volatility render them extremely difficult to dry off. Drag out losses are very high. As for HCS processes, these may reach as much as 4 $g.dm^{-2}$ on densely populated SM circuits, even with air-knife excess solvent removal. Energy consumption for drying may be very high with solvents whose boiling points exceeding about 135°C.

2.4.5.1 Light HC solvent processes

This is occasionally used for very small scale cleaning (i.e. circuits), using open trays and brushes. They represent distinct fire and toxicity hazards. For full production scale cleaning, machines with appropriate flameproofing, including nitrogen purging, are available. For correct cleaning quality, many light solvents, including alcohols, saturate at extremely low levels of heavy metals, particularly lead salts. This means that heavy-duty reflux distilling of the solvent is necessary to ensure enough pure material is present for the last rinse. This is a very costly process.

Advantages:

- Low-cost solvents
- Generic solvents readily and universally available
- Easy-to-repurify by reflux distillation

Disadvantages:

- High capital cost for machinery
- High energy requirements
- Good cleaning quality difficult to ensure consistently
- Anti-fire/explosion precautions costly
- Solvents are VOCs

2.4.5.2 Heavy HC solvent processes

These are arbitrarily separated from light solvent processes when the boiling point of the solvent exceeds about 120°C and the flash point is higher than about 50°C.

Those based on ethylene diglycol type derivatives (also usable as miscible HCS solvents) are very effective cleaners without much evaporative loss. However, they have an extremely low vapour pressure, with flash points often in excess of 100°C. This renders them very difficult to dry off. Tests with one type have shown that such solvents may require time and energy requirements greatly exceeding those of water under the same conditions by a factor of five or more (Scolari 1993). Drying temperature should be limited to at least 20°C under the flash point. The drying process may be aided by a final perfluorocarbon vapour phase stage (2.4.6) but this is not recommended due to the emissions of global warming gases. The process may consume high quantities of solvent by drag-out losses.

Advantages:

- Good cleaning quality possible
- Low fire hazard
- Low toxicity (some products)
- Easy to handle and use
- High rosin loading possible

Disadvantages:

- Expensive solvents
- Difficult and expensive drying
- VOCs
- Difficult to repurify and recycle the solvents

2.4.6 Permitted halocarbon processes

There are three halocarbon processes which may be mentioned, using non-ozone depleting chlorinated solvents, HCFC and HFC blends and PFC drying processes.

All three of these processes demonstrate grave environmental and other disadvantages. Practical experience in many locations have shown that there are very few cases where the use of these environmentally disadvantaged products present a real benefit over more benign processes for the electronics industry, either economically or technically.

At best, they can offer only a temporary, technically doubtful and costly alleviation of the problem. Most of those companies in the electronics industry that have adopted them have chosen HCFCs and they are generally aware that this process is temporary and may not be either entirely suitable or economically viable. However, it may offer them the time necessary to choose a more suitable process.

2.4.6.1 Non-ozone-depleting chlorinated processes

Theoretically, all chlorinated solvents are ozone-depleting, although a number of them have negligible ozone-depleting potentials. These include perchloroethylene (tetrachloroethylene) and trichloroethylene. Solvent blends containing perchloroethylene have been proposed as "cold flux removers". To date, there is no evidence that these offer any real technical advantage over other processes. On the other hand, they are known to cause problems with many synthetic compounds such as a number of plastics and even printed circuit substrates. As a result, their use is relatively limited. They have occasionally been employed with "kiss" cleaning machines (bottom-surface brushing machines) to remove sufficient flux to allow automatic test machine probes to contact the metallic surfaces, without truly cleaning the assemblies, but this is a niche market, possibly better resolved by using certain qualities of "No-Clean" flux.

Advantages:

- Easily obtained, low-cost solvents
- Zero-to-low ODP
- Traditional method

Disadvantages:

- Health and safety concerns
- Some blends may be VOCs and/or have high GWP
- Cleaning quality often mediocre
- Plastics and PCB substrates often sensitive to solvent
- "Cold" cleaning produces high drag-out losses
- "Cold" cleaning blends non-azeotropic
- High boiling points preclude vapour defluxing in some cases

2.4.6.2 HCFC Solvent processes

Except for the very rare application, HCFC solvents should never be used for cleaning an electronics assembly.

All HCFCs deplete the ozone layer. They are regulated under the Montreal Protocol and those controls may become more stringent until a total phaseout is achieved. Two HCFC solvents are otherwise suitable for electronics cleaning. HCFC-141b has a high ODP (comparable with that of 1,1,1-trichloroethane) and may be subjected to more severe restrictions in the short term. It also attacks many plastics materials and has a low boiling point with a high volatility. This is the least recommended of HCFC solvents for this work. HCFC-225 is a blend of isomers and has characteristics quite similar to CFC-113 except for a lower ODP and a higher cost. It is the nearest solvent we have to a "drop-in" replacement of CFC-113, even to the extent of blends with similar characteristics.

The equipment, when using HCFCs, must always be suitable to minimise emissions. This is not only to prevent unnecessary ozone depletion, but also from a purely economic standpoint as the cost of these solvents is high. Any unnecessary losses therefore compromise their economic viability. Above all, they should never be used in an open-top vapour degreaser, particularly if the model is more than two years old.

Advantages:

- Process similar to the familiar CFC-113 vapour defluxing

Disadvantages:

- Ozone depleting
- Some blends may be VOCs and/or have a high GWP
- Requires expensive near-zero emission machinery
- Forbidden in some nations
- Future legislation uncertain in some others
- Some solvents expensive
- Doubtful economic viability
- Cleaning quality doubtful (according to solvent)
- Attacks some plastics (according to solvent)
- Transitional substances only

2.5 MACHINERY FOR ENVIRONMENTALLY RESPONSIBLE SOLDERING AND CLEANING

All electronics soldering and cleaning is detrimental to the environment. It is important that those selecting equipment choose types suitable to do the required work, yet cause a minimum amount of environmental harm. This section will give a brief review of some of the risks that occur with different process types.

2.5.1 Conventional wave soldering

While wave soldering is generally not a very polluting process, it is not entirely benign either. The worst pollutants are those derived from the flux during the preheating and soldering stages. The fluxes generally contain organic solvents, usually light alcohols. These are evaporated, mostly during the preheat stage, but residual amounts during the actual soldering. There is little decomposition of these compounds which are usually almost 100 percent emitted. They are not very dangerous to the environment, due to their hydrophilic nature which gives them a very short atmospheric lifetime. However, a few nations or regions do consider them as VOCs. The cheapest way of reducing their emissions is to use cold water, in a small scrubbing tower, between the machine exhaust and the outside air. The resultant water/alcohol mixture may then be treated to separate the components and thus recover the alcohol (this is not necessarily an economical recovery).

Also from the flux, activators and vehicles are often volatilised, sometimes unaltered, sometimes decomposed, as well as the solvent system. These may be hydrohalide acid gases, amines and amino acids, linear or cyclic carboxylic acids, oxygenated hydrocarbons or derivates of these substances. Rosin, for example, may partially decompose into toxic aldehydes. In particular, Low-Solids "No-Clean" fluxes are often designed to deliberately volatilise or sublime so as to minimise the quantity of post-soldering residues. All these products, with the exception of hydrohalide acid gases, must be considered as VOCs. The quantities emitted per machine may not be very large, but the global emissions must amount to thousands of tonnes per year. Some products may even be considered as toxic or otherwise dangerous to the environment. Again, a water scrubber will reduce effectively the quantity of pollutants emitted, followed, if necessary, with an active carbon filter.

A third class of pollutants derived from wave soldering are metal oxides and salts. Tin and lead in the solder wave oxidise on the surface. This film of oxides falls into the solder bath, breaking up as it does so. Turbulence at the surface causes a small quantity of these oxides to be projected as an aerosol dust into the air. If there are flux activators in the air, as well, these oxides may be reduced into metal salts, some of which, finely divided, may be particularly toxic, even if the quantities are almost infinitesimal. Again, a water scrubber will remove most of this kind of particle, but the water may require more rigorous treatment.

Metallic particles, often termed microspheres or microballs, are frequently produced in relatively large quantities and may adhere to the surface of the board. These are mostly removed in subsequent cleaning and may cause problems in the cleaning product if not carefully mechanically filtered.

2.5.2 Controlled atmosphere wave soldering

The pollution produced from controlled atmosphere wave soldering is generally very similar to that from conventional soldering, except that the oxidation of the solder is much reduced. There is therefore relatively little metallic salt formation. The quantity is not reduced to zero, because of the oxides present on the board and component leads before the soldering process commences. These are not completely reduced to salts before the passage into the wave, so a finite amount of dross is always present. Microballs are also more frequently produced with this process but, as the boards are rarely cleaned, they do not represent a major hazard in the cleaning process, even if they may cause electrical problems. A newly developed controlled atmosphere soldering process uses a reducing gas plasma in place of fluxing. It is not yet sure to what extent this can reduce organic contaminants on the components without attacking the organic substrate.

2.5.3 Infra-red etc. solder paste reflow

This section also includes most other types of reflow, with the exception of vapour phase and liquid immersion types. The pollutants produced are generally similar to those produced by wave soldering. In addition, chemical agents in the pastes to establish the right rheological characteristics add to the spectrum of evaporated chemicals. These may take numerous forms but all such emissions must be considered as VOCs.

2.5.4 Vapour-phase solder paste reflow

This is possibly one of the worst pollution generators in the electronics industry, after CFC-113 cleaning. There are several conceptions of the process, but none are better than the others. Fortunately, it is losing popularity and few new equipments are being put into service.

The main problem with this process is analogous to that of CFC-113 cleaners. A heavy vapour is used to allow the parts to reach the soldering temperature. This vapour is not easily contained and the methods used to contain it often acerbate the problem. The vapour is a perfluorocarbon (PFC) compound with a boiling point in the range of 215°-260°C. As far as is known, PFCs have no effect on the ozone layer but they are among the worst "greenhouse gases". Furthermore, they have atmospheric lifetimes of 500 to 10,000 years. The breakdown mechanisms are unknown and there is a finite risk that they may cause unforeseen problems within a few centuries if allowed to accumulate in the atmosphere. For this reason alone, this process is not recommended.

There are three major methods used to reduce emissions of the expensive PFC reflow medium, none of which are completely effective, as the medium is often entrapped under the components on the assembly. These are the mechanical machine design, the use of a CFC-113 secondary vapour blanket and the use of a more volatile, less expensive, PFC secondary vapour blanket. The latter has only an economical effect, as the PFC used for the blanket is as bad a "greenhouse gas" as the primary vapour. CFC-113 is, of course, not acceptable because it is a regulated substance under the Montreal Protocol. No economical machine design can reduce the emissions of the PFC to an effective level.

2.5.5 Hot liquid immersion solder paste reflow.

This method uses a glycol derivative heated to the fusion temperature as the heating medium. It has a number of advantages, especially for thick film circuits. A good proportion of the paste residues actually dissolve in the medium, so that the cleaning process, using a simple water wash, becomes easy.

The medium starts to decompose fairly rapidly, evidenced by a visible carbonisation, but this does not become serious until the end of the useful life of the product, typically 30-40 hours at the reflow temperature. Even though the vapour pressure of the medium is so low at room temperature that it may not even be considered a VOC, the evaporation at fusing temperature is quite high. This will contribute to tropospheric ozone and smog under the right weather conditions. The process is quite dirty as a sticky polymer tends to condense all around the machine. This makes a good extraction system essential, designed to minimise cooling at the liquid-air interface. The extracted air can be water-scrubbed: mechanical filters are useless as they clog very rapidly. The water in the scrubber tower may be contaminated to a heavy degree but may be used as the first wash water for the reflowed assemblies. The contaminated water will have a high BOD_5 and some authorities may not permit its discharge into sewage. The heavy metal content may be acceptable as much of the metal salts will remain in the fluid. This would require analysis before allowing it to discharge.

The spent fusion fluid must be considered as a hazardous waste and be disposed of correctly. Apart from the heavy metals, the product will have become heavily decomposed and polymerised. It will be largely non-biodegradable, either in water or soil. It cannot be effectively used as a fuel unless the metal content is removed and the residues cracked to lighter hydrocarbons. This can be a severe limitation to its use.

The paste type used in this process is usually water-soluble. Rosin will dissolve reasonably well in most of the commercial fluids, but an accumulation of rosin residues will reduce the useful life of the product and make it even more difficult to eliminate.

2.5.6 Aqueous cleaning (conventional water-soluble fluxes)

The first wash water of straight water washing will contain heavy metals, usually to prohibitive levels. Its pH may also be lower than is permitted by many authorities. It will also contain glycols and surfactants which will both increase the BOD_5, but generally not to severe levels with the levels commonly formed. The water may be treated by any conventional method to remove the metal content and neutralised with a basic solution. This would allow the waste water to be discharged, assuming the biodegradability was acceptable.

Complete recycling of the waste water is nearly impossible: the maximum is probably about 75 to 80 percent, in most cases. The remaining 20 to 25 percent represents drag-out losses, evaporative losses, membrane concentrate solute, diverse filter replacement losses, deionising column regenerating solution and rinse waters and other water usage. Any water treatment using membrane or deionising techniques to remove heavy metals does not really help the situation: at the best, it displaces the problem to another level, as the metals are still present either in the concentrated waste water and in the resins. On regenerating the latter, the metal is removed and re-enters into an aqueous solution. If the resins are mixed bed, this is usually done off-site and the regenerating station must be warned that heavy metals are present. The one advantage in concentrating the heavy metal salts in waste water is that they become easier to treat than in a highly diluted form.

2.5.7 Aqueous cleaning (glycol-free water-soluble fluxes)

The environmental problems with so-called glycol-free fluxes are identical to those of conventional water soluble fluxes. Despite the term "glycol-free" some fluxes of this type do contain certain benign glycol derivates, even if they do not contain the polyglycols suspected of causing a reduction of surface insulation resistance of some substrates. Some of the surfactants used to allow such fluxes to foam or to improve the wetting of the flux are very closely related to some of the polyglycol derivates.

Some of these fluxes also contain tribasic carboxylic acid activators, such as citric acid. These are known to have a chelating action on heavy metal salts. As a result, the latter may be more difficult to remove until such time as the acids start to biodegrade, which may take a considerable amount of time.

As a general rule, these fluxes are no better environmentally than their conventional counterparts, as far as the cleaning process is concerned, and may present greater difficulties.

2.5.8 Saponifier cleaning

Saponifiers based on monoethanolamine operate normally at around 55°C. At this temperature, there is a certain amount of evaporation of the amine and the co-solvents. The latter are usually VOCs, but the amines, being basic, tend to react rapidly with acid gases, such as carbon dioxide, especially in the presence of humidity. Because of this, their atmospheric lifetime usually is very short. The reaction products are generally without effect, being also very hydrophilic with a very short folded-e lifetime. They may form nuclei for mist formation if the atmospheric humidity approaches saturation. This must not be confused with ozone and smog formation due to the photochemical reaction between nitrogen oxides and VOCs.

2.5.9 HCS solvents

HCS solvents may be among the most polluting methods of cleaning. Practically all the solvents are classed as VOCs at normal operating temperatures. Most of the emitted vapours can be collected from all parts of the machine (including the wash and rinse sections and the separator, if so equipped) and economically reduced by a water scrubber.

The most polluting aspect of the HCS processes is the quality of the wash and rinse waters. Even if gravitational and/or membrane separation techniques are used, a considerable quantity of solvent remains either in the water when the machine is drained and the concentrate contains considerable proportions of water. Many commercial machines, including some quite large and expensive ones, are equipped with no means of separation, meaning that most of the large quantity of dragged-out solvent ends up in the waste water. This is especially critical with solvents that actually form a stable mixture with water, where no economical form of separation can possibly work, except for the very largest installations. One commercial machine, designed for use with a high-boiling point solvent, developed in Great Britain, concentrates the mixture by evaporating off the water. However, this is inefficient and energy-intensive: as some of the components of the solvents, themselves zeotropic, form an azeotrope with water, the resultant residue contains water and has a composition wildly different from that of the original solvent. It is likely that the recovered solvent is not extensively re-usable and that considerable quantities of some of the components are emitted.

Solvent drag-out losses can be very high, of the order of 100-500 g/m^2 of printed circuit assembly depending essentially on the type and density of the electronics components. Many machines are equipped with air knives on exiting from the solvent phase of the cleaning process. This is insufficient to significantly reduce the problem: if the energy is sufficient to eliminate more than a few percent of the solvent residues, most of the solvent will be atomised or vaporised, thus displacing the problem from water to air. In practice, with a machine which air-knives the PCBs without causing undue losses, only the superficial solvent, representing typically about 50-100 g/m^2, will be recovered.

The solvent in the wash water is usually claimed by the manufacturers to be "biodegradable". In reality, many HCS solvents have a very high BOD_5 and or COD, sometimes exceeding national limits or recommendations even in small proportions. This aspect should be carefully examined before choosing such a process or, at least, a given solvent.

Even if gravitational separation is employed, practically all the surfactants -- often up to 10% of the solvent volume -- and dissolved heavy metals remain in the water. The only way to improve separation is by active carbon filtration to handle the large quantities of surfactant followed by traditional methods of deionisation or precipitation to remove the metals. Membrane techniques may not be able to separate the two pollutants from each other.

The most difficult problem is the disposal of the used solvents. These contain, as well as the original components, heavy metals, rosin residues, activators and other contaminants resulting from the assembly being cleaned. They are therefore considered toxic waste. Since about one-third of such waste is composed of contaminants from the assemblies being cleaned, the composition is completely unknown and the heavy metal content is likely to be quite high. The *only* safe way to dispose of these products is to incinerate them in a kiln designated for the disposal of combustible chemical waste. There exist a handful of special purpose-built kilns for this throughout the world, but their use is expensive. More usual is to mix the solvent into cement kiln fuel with *approved* installations. Most of the incombustible residues (heavy metal salts) are incorporated in minute proportions into the cement. They do not alter the cement properties and they eventually become encapsulated in a mass of solid cement or concrete where they are harmless. The remainder of the salts are collected by the fly ash electrostatic precipitator whose contents are usually added to the limestone feeding the kiln. Any acids or other volatiles from decomposition of the activators are collected in a water scrubber mounted in the flue.

Some manufacturers of HCS solvents try to make light of the disposal problem of the used product. For example, it has been suggested that the spent solvent may be added to heating fuel oil. The problems that could result from such advice may be:

- *clogging of the burner nozzles by burnt rosin, causing poorly controlled combustion*
- *acid vapours could attack burner parts, boilers and flue linings if they are of unsuitable materials*
- *all the heavy metal salts would be emitted into the atmosphere*
- *the optimum fuel:air ratio will be upset producing excessive emissions of NO_x gases and soot*
- *in summer, when the fuel consumption drops, the problem tends to become acerbated by excessive quantities of solvents*

This practice, where it is not expressly forbidden by law, should be discouraged.

2.5.10 HC solvents and derivatives

As a general rule, all straight solvents are VOCs and their disposal must be done according to the criteria of common sense. Both these subjects form part of the last section (2.5.9) and their treatment is more-or-less identical. They normally engender no water pollution problems, by definition.

The only exception to this is with the use of light solvents, such as the lower alcohols. The vapours from these form a distinct fire and explosion hazard, as well as being VOCs. Appropriate action should be taken, in conjunction with the local fire protection agency and insurance company, to prevent any emissions from creating an unforeseen hazard. The best method is to ensure that the emissions are as low as is humanly possible.

2.5.11 Permitted halocarbon solvents

No matter their composition, all halocarbon solvents are dangerous to the environment, being any combination of ozone-depleting, global-warming, toxic, VOCs and generally undesirable. It is the responsibility of the user to reduce their emissions to virtually zero at all times by suitable machine design and housekeeping practices. There is really no reason why they should be used for any purpose within the electronics industry, with the possible exception of a very few minor applications, representing perhaps the production of one establishment in tens of thousands.

Unfortunately, this is unrealistic. There has been economic pressure to use HCFC-141b in place of CFC-113. Some vendors claimed that it could be used in existing machinery without modification of the equipment or the working practices. The result was that emissions into the atmosphere increased significantly. Although this solvent has only about one-fifth the ODP of CFC-113, the net result would be the unnecessary emission of an ozone-depleting substance. As HCFC-141b mixtures are poor defluxers and can attack some electronics components, there is no reason why it should be used for this application. If, for any reason, an HCFC solvent must be used for defluxing, then an HCFC-225 mixture would be more suitable. Also, since it is more expensive, users will have the incentive to minimise emissions.

The Solvents, Coatings and Adhesives Technical Options Committee does not recommend HCFC-141b for defluxing in the electronics industry under Multilateral Funding[8].

The measures to be taken to minimise emissions of HCFC-225 and other halocarbon solvents are described adequately in past editions of these reports (UNEP 1989, 1991).

2.6 PRODUCTION MACHINERY AND MATERIALS

The choice of machines for assembling and soldering printed circuit boards is too large to catalogue all that are available. Instead, discussion will focus on the impact they may have on the overall process when substituting new methods for traditional ones.

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[8] HCFC-141b has a high ozone depletion potential (ODP) of 0.11 which is equivalent to the 1,1,1-trichloroethane ODP of 0.12 and it is controlled under the Montreal Protocol. Future changes may further restrict its use or advance its phase out dates. HCFC-141b should therefore only be considered as a replacement for CFC-113 in specialised application where no other substitute or alternative exists.

2.6.1 Conventional wave soldering machines

When choosing a new wave soldering machine or adapting an existing one, it is important to look at the means for fluxing. Traditional rosin fluxes usually foamed very well, so that foam application was the choice of predilection. This was simple, effective, and inexpensive. Originally, air was pumped in through a porous, cylindrically shaped stone. To obtain more uniform results, this was replaced by synthetic sintered stones. Some of these were slowly attacked by some fluxes and sintered plastic "stones" are now the rule, being cheap and long-lasting. They are available in different pore sizes and the choice may become critical according to the flux characteristics with modern fluxes.

As a general rule, "No-Clean" Low-Solids fluxes do not foam very well and are sometimes difficult to use in a foam fluxer. If problems are experienced, one should try different stone porosities. Having determined the best one, if the foam head is still inadequate, it may be necessary to modify the chimney geometry with either a new chimney or polypropylene inserts, fashioned to suit. These should restrict the form to as narrow a chimney as possible, 6-10 mm internal width at the top and 2-3 mm more than the stone diameter at the bottom being ideal.

Another approach is to replace a foam fluxer with a fine plastic mesh drum which turns with the bottom third in the liquid flux. At the top, an air-knife blows the flux held by capillary action as fine droplets onto the board. This is possibly more reliable than foam fluxing in difficult cases.

In both of the previous methods, there are considerable changes in the flux composition with time, as the air used exaggerates the evaporation of solvents and may add humidity to the flux. The solvents have to be replaced to maintain the correct flux characteristics. With conventional fluxes, this replacement can be calculated and checked easily by simple gravimetric means. With Low-Solids fluxes, this is not possible as the difference in density between the flux and the solvent is small and the results can be easily misinterpreted by the presence of humidity absorbed from the atmosphere or the air used in the fluxer. The only reliable low-cost method is by titration and some flux manufacturers provide simple titration kits for use with their fluxes for maintenance.

Another fluxing method is to spray the flux evenly over the board using oscillating or multiple spray heads. These must produce a fine, uniform deposit without undue quantities of mist which would not only be wasteful but also present an explosion hazard. Ultrasonic spraying, for example, is considered as an excellent means for this method. This has the additional advantage that the flux that is sprayed is always exactly of the "as-delivered" composition and no maintenance is required.

Fluxer materials must be compatible with the flux being used. In Europe, the traditional fluxer material is stainless steel. This has proved to be inadequate for use with some water-soluble fluxes, which can attack it, especially along the welds, over a period of time. Early US fluxers were frequently made from fabricated PVC sheet. This material resists most fluxes very well, with the exception of those containing esters in their solvent system. Perhaps polypropylene, which is also cheap and easy to fabricate, presents the best compromise.

The machine should be fitted with an air-knife immediately after the fluxer. This serves three purposes:

- it removes excess flux and pushes it back into the flux reservoir or a catch tank
- it ensures a more even flux distribution
- it helps flash off the excess solvents, easing the load on the preheater.

Preheating is the next critical point. Some European machines are inadequate in their preheat temperatures. The preheating is often thought of as simply to evaporate the solvents in the flux, although this is not true. It has to bring all the parts of the board and components to be soldered to a temperature at which the flux can reduce any oxides present before contacting the wave, so that the molten metal can immediately start forming intermetallic compounds. This temperature may depend on the flux type and the nature and quantity of the activators. As an approximate rule, this critical preheat temperature is generally in the range of 90°C to 115°C. As it is expected that the solder should rise in plated-through holes, this should be measured on the *top* side of the assembly being soldered at the instant immediately before entering the wave. Temperature profile recorders are ideal for determining this. These are small devices with a number of thermocouples on flying leads attached at appropriate points to the assembly. The whole device is passed through the machine and afterwards the results, held in memory, are analysed and printed out. There are excellent devices of this nature manufactured in Europe and the USA.

The method of preheating employed is often unique to particular machines, ranging from convected air to forced hot air and from low-temperature hot plates to electric light bulbs, or combinations thereof. There is no ideal method, provided that the required temperature can be achieved in the minute or so of preheating. However, particularly when using Low-Solids fluxes the infra-red absorption characteristics of an assembly can vary widely according to the peak wavelength of an infra-red generator. Metal is heated much less efficiently as the wavelength increases so, if the desired temperature is reached on the top side of the circuit from a very brightly incandescent source, there is a very real risk that the substrate will become too hot, causing discoloration, chemical decomposition or an unusual 'set' due to the glass transition temperature (T_g) being exceeded for too long a time. Experience has shown that the most usual method employing metallic (Inconel) Infra-red heaters at temperatures within the range of 400°C to 700°C in a polished reflector or some hot air types give the best results.

Energy consumption is also a factor where, ideally, all the heat generated should be converted into a rise of temperature of the PCB. More important than the actual conversion efficiency is the conservation of energy in stand-by periods. With incandescent and hot-air preheaters, they can be switched on as and when needed and switched off when there are no boards being processed. With metallic or ceramic infra-red heaters, these should be as thin as possible to minimise thermal inertia. They can then be switched on for all the time there is a board present as from the entry of the machine (to ensure they are at full working temperature by the time the board reaches the preheat zone) and switched off again a few seconds before the last board quits the preheat zone. To achieve this ultimate performance, sophisticated temperature controllers using proportional techniques with differentiation and integration are required, with a sensor wire in the heater itself. These apply full power to the heater during warm-up to reach the working temperature very rapidly. About 5°C before reaching the preset heater temperature, the power is progressively diminished until it reaches optimum at which temperature the whole system is in perfect equilibrium with no overshoot. The moment the temperature varies from optimum, the power is adjusted accordingly to reestablish the perfect conditions. The controller can even anticipate in advance the conditions needed to perfect the temperature control without any overshoot or excessive damping.

As well as "No-Clean" fluxes, low VOC fluxes are particularly critical in terms of preheating. They usually contain a considerable percentage of water which requires much more energy to evaporate before the board can be brought up to the full preheat temperature.

The design of the wave is also particular to many manufacturers and should be of little consequence in the final results.

One exception to this is that of double waves. This technique is designed to ease soldering of "glue-spotted" surface mount devices. It consists of having two separate waves or a single wave divided into two zones. The first wave is purposely highly turbulent, designed to project the molten solder into the shadows created by the components, allowing initial wetting in these zones. The second wave is smooth and is designed to ensure that the wetted areas form a bright, even and smooth meniscus. There is a hic with this technique. For it to be successful, there must be sufficient flux available to reduce oxidation at the second wave. With conventional fluxes, this is no problem. With Low-Solids "No-Clean" fluxes, there is sometimes insufficient flux remaining after the passage over the first wave to ensure correct smoothing in the second wave. This implies that, at least, medium solids (about 8-10 percent) fluxes should be used although some engineering changes may help considerably with lower solids materials. This is not always compatible with all the "No-Clean" criteria.

Because soldering with modern fluxes is often more critical, with narrower operating windows, than with conventional fluxes, everything should be done to ensure ease of soldering. This means tightening of operating tolerances. In previous operations, solder alloys with tin contents as low as 40% were successfully used. Only binary or ternary eutectic alloys, such as 63%Sn/37%Pb or 62%Sn/36%Pb/2%Ag should be considered with Low-Solids "No-Clean" fluxes. The soldering temperature is also more critical with these fluxes and should be chosen within the range 230°C to 250°C after practical trials.

Optimisation of the soldering process is tricky, as there are many input and output parameters. Some form of scientific evaluation is usually necessary, especially with "No-Clean" techniques, to bring the trial procedures within reasonable bounds. One of the easiest ways of doing this is with the Taguchi method whereby eight input variables and any number of output variables can be analysed with only twelve experiments, followed by a thirteenth confirmatory experiment after the analysis. For example, the input variables could be:

1. Percent flux solids (2-6%)
2. Flux wet weight:area ratio (0.3-0.7 $g.dm^{-2}$)
3. Conveyor speed (0.9-1.5 $m.min^{-1}$)
4. Preheat air temperature (180°C-220°C)
5. Radiant heater temperature (400°C-500°C)
6. Solder temperature (230°C-250°C)
7. Solder resist (dry film or wet film)
8. PCB metal treatment (HAL or IRR)

The output variables could be:

1. Defective solder joints
2. Bridges between joints
3. Other bridging
4. Insufficient rise in PTHs
5. Skipped pads
6. Aesthetically unacceptable or uninspectable joints
7. Solder webbing
8. Visible residues
9. Residues causing AT probe problems
10. Surface insulation resistance etc.
11. Number of less-than-minimal menisci
12. Number of more-than-maximal menisci

Each of these output variables can be weighted in terms of their individual importance or the list lengthened or shortened at will, without changing the number of experiments, inasmuch as boards evaluated for one criterion are suitable for evaluating all the other criteria.

Commercial software is available for helping in Taguchi optimisation.

2.6.2 Controlled atmosphere wave soldering machines

These are essentially the same as the machines discussed in section 2.6.1 (q.v.)

In reality, only inert gas is used in commercial systems, the gas being generally nitrogen. Reactive gases have been tried, as well as mixtures of inert and reducing gases. Soft soldering does not reach temperatures where reducing gases, such as hydrogen, are really effective. For this reason the reactive gas technique is not common.

There are three basic techniques used to ensure the soldering zone is inerted:

- a tunnel adaptation of conventional machines
- purpose-built tunnel machines
- purpose-built hermetic machines.

The first is cheap to install and reasonably effective. However, it is more difficult to ensure the complete purging of air around the soldering and preheating zones, an essential element of the technique. Practical tests indicate that best results are obtained when the oxygen content is reduced to 6-10 ppm, but satisfactory results have been obtained at higher levels of oxygen. To achieve this under these conditions is very difficult and requires heavy nitrogen consumption, making it an expensive option in terms of operating costs.

Purpose built tunnel machines use clever gas curtaining and other techniques to reduce the admixture of air into the soldering and preheating zones without excessive gas consumption. Notwithstanding, the consumption still remains quite high.

Purpose-built hermetic machines avoid any risk of contamination of the nitrogen by air. The assemblies being processed pass through airlocks at each end of the machine. The air in them is evacuated twice and replaced by nitrogen before they are opened to the interior of the machine. This is much more economical to run, but slightly higher in capital costs.

These machines are typically designed around the use of special fluxes, sometimes commercially named preparation fluids. Early Inert-atmosphere fluxes were simply dilute solutions of adipic acid in isopropanol. New Inert-atmosphere fluxes are appearing on the market which are claimed to have more benign and/or lesser quantities of residues. One is claimed to leave even a completely inert polymeric coating over both surfaces, giving additional protection. When the quantity of residues diminishes, the metal salts produced by reaction between the flux activators and oxides present on the components are more exposed to the effect of atmospheric conditions in service. Their effect on the reliability of the assembly is still undetermined.

Some inert-atmosphere machines provide the option of injecting a formic acid mist in the soldering zone, which may be dangerous. Theoretically, formic acid volatilises at about the same temperature as water and decomposes into carbon monoxide (the reducing agent) and water at soldering temperature. For it to be innocuous, it would be necessary to ensure complete removal of the acid from the assembly. This implies that the whole assembly would need to be taken to soldering temperature, including the upper surface of the components, to ensure that any formic acid was totally decomposed and that all parts of it remained at over 100°C during the whole sojourn in the soldering zone to prevent formic acid from condensing back onto it. Neither of these conditions can be guaranteed and independent tests with and without formic acid injection have shown that the residual ionic contamination may be up to three to four times higher with the injection than without it.

Various contradictory statements have been published as to whether Inert-atmosphere soldering is economically viable, compared with traditional wave soldering. This is not surprising, as individual conditions are so variable. Unless a machine is used to near-full production capacity, preferably 24 hours per day, then it is possible that the cost of amortisation and keeping it idling (nitrogen consumption) may become prohibitive. The savings due to lower dross formation are often very small and are offset by the nitrogen consumption necessary to achieve it. A recent communication even suggests that hidden costs involved in inert-atmosphere "No-Clean" soldering may actually make it uneconomical.

Inert-atmosphere wave soldering has a very narrow operating window and is very difficult to master during initial set-up. It may require the use of selected solderable components. Once the process has been optimised, the retouch rate should not be much higher than that from other processes. The switch from a traditional machine to an inert-atmosphere machine can be a lengthy process. An overlap period with both machines in service in parallel of at least 4-8 weeks is generally necessary. Again, Taguchi optimisation can be a quick and reliable help to putting such a machine into service.

2.6.3 Vapour phase reflow

Vapour phase reflow will not be discussed due to the decrease in its use. This method also results in the emission of "greenhouse" or other highly polluting gases including, in some cases, ozone-depleting blanket gases.

There are no known applications whereby some other means of reflow would not give equal or better results, usually at lower cost. One critical application is for reflowing components on certain complex flexible circuits. The non-directionality of vapour phase reflowing made it technically attractive for this. Careful jig design is usually sufficient to allow hot air or infra-red reflow to be equally successful.

The Solvents, Coatings and Adhesives Technical Options Committee does not recommend vapour phase reflow in the electronics industry, under the terms of Multilateral Funding[9].

2.6.4 Infra-red reflow machines

There is a wide choice of machines available, from simple "simmerstated" Infra-red heaters over a moving conveyor to very complex multi-zone machines with individual inert gas purging of each zone, mixed heating methods and sophisticated process control. It is therefore impossible in a few brief paragraphs to give more than an outline of the process.

The most common process is to stencil or screen solder paste onto the PCB to be processed, force the components onto the wet paste and then reflow the paste to achieve good soldered joints.

The paste itself is (usually) an intimate and fairly homogeneous mixture of minute spheroids of solder alloy in a chemical mixture. The spheroids are carefully size-graded and the most popular grades approximate around 50 μm diameter. Special purpose pastes may have smaller or larger particles. It is important to note that smaller particles would appear to approach the ideal, but they do have more surface area per unit weight of metal, hence any oxidation becomes greater in proportion to the metal mass and the paste becomes more difficult to use with a shorter lifetime. The metal to chemical ratio is typically in the range of 85-95 percent of the total weight, but the ratio is about only 50 percent by volume. It is important to realise this, as the quantity of chemicals is much greater with reflow than with wave or hand soldering (solder wire usually contains only 1-3% flux by weight) and the quantity to remove thereafter is also much greater. The chemicals themselves are a small quantity of flux and, proportionally, much larger quantities of thixotropic gels and other rheological agents, heavy molecular weight solvents etc. This mixture of chemicals is very complex and the role that each component plays during screening/stencilling, holding, component placement, holding again, preheating, reflowing, holding a third time and cleaning (if done) must be studied during the formulation. The ideal paste would be a completely inert mixture that could be screened perfectly without any slump, with an indefinite open time on the screen, have an indefinite hold time, would cause instant and perfect adhesion of placed components, could be held indefinitely without humidity absorption, could be preheated and reflowed without fault over a wide range of temperature profiles, wetting oxidised components, and maintaining perfect adhesion of them during the process, and then leave no chemical residues or solder balls whatsoever. This fiction does illustrate that the preheat/reflow process is only a small part of the total process and cannot be taken in isolation.

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[9] All vapour phase reflow processes emit PFC vapours. These may be the subject in the future to restrictive legislation designed to curtail emissions of "global warming gases" which may be a cause of climate change.

The main problem with Infra-red reflow of pastes that are destined to be cleaned is the importance of ensuring a perfectly controlled thermal reflow profile. A recorder of the type mentioned under wave-soldering machines is a certain asset in ensuring this. The various components of the chemicals used inter-react with each other as well as with what it contacts on the components and boards. The result is a mixture whose composition is difficult to determine. Even a slight change of fusion temperature and/or time may render the residues totally impossible to be removed. This is more important with pastes that leave thick deposits, such as common, general-purpose RMA and RA pastes. Careful control of the fusion process is therefore very important when reflowing this kind of paste, and sophisticated equipment must be used.

Modern "No-Clean" pastes rely on the volatility of their major components at fusing temperature to minimise the quantity of visible residues. It is important that at least a thin film of flux remains until the solder solidifies, to ensure acceptable menisci. Some require the use of a controlled atmosphere, either inert or active. For best results, manufacturer's recommendations should always be closely followed.

As the major part of "No-Clean" pastes does volatilise, the user should be aware that a large facility could emit significant quantities of VOCs unless precautions are taken to capture them. This is not commonly realised and many plants violate VOC emissions laws. The same holds true for some wave soldering fluxes, even low-VOC types, but the quantities of activators which evaporate involved are relatively small. The term "low-VOC" means that most of the solvents have been replaced with water and does not refer to the activators which are always VOCs at soldering temperature. With pastes, up to 90% of the chemicals, representing typically 45% of the volume of the bought-in paste, are organic chemicals which, sooner or later, volatilise during processing.

2.6.5 Other reflow methods

There are a number of alternative methods of reflow used. These include thermode, hot gas or air, laser, non-coherent focused flash radiation, hot belt (mainly ceramic substrates), liquid immersion, and the old soldering iron. These will not be discussed here, as they are of limited interest and their advantages and disadvantages related to cleaning are logical extensions of the previous sections.

2.7 CLEANING MACHINERY

There are many different types of cleaning machinery and features within specific types. The following summaries are therefore broad and the user is warned that they are not comprehensive. Auxiliary features, such as waste water treatment, are not considered in these lists. The term "drag-through" is used here to describe liquid that remains in a machine from one operation to the next, as opposed to drag-out which is liquid that remains on the workpieces from one operation to the next.

2.7.1 "Dishwasher" types

"Dishwasher" types of batch machinery are available for use with some solvents (including some HCS solvents), some emulsion cleaning and most forms of aqueous cleaning. *It is important to note that unmodified domestic or industrial dishwashers are unsuitable for cleaning electronics assemblies for many reasons.*

Advantages

- Low capital cost
- Small floor space "footprint"
- Cleaning quality may be excellent
- Some may be purged for flammable/combustible solvents

Disadvantages

- High energy and pure water requirements per unit area
- Very low throughput capacity (typically 1 $m^2.h^{-1}$)
- Drying quality may not be perfect
- Optimisation of wash and rinse cycles difficult
- Machine drag-through high
- Saponification may be difficult
- Handling of heavy baskets at a low level

2.7.2 "High-Throughput" types

"High-Throughput" types of batch machinery are available for use with some solvents (including some HCS solvents), some emulsion cleaning and most forms of aqueous cleaning. They are characterised by separate machines or compartments for cleaning and drying, separate optimised wash and rinse circuits for cleaning and rotary high-speed hot-air knives for drying.

Advantages

- Will accept output of most soldering machines (20 $m^2.h^{-1}$)
- Very efficient cleaning
- Very efficient drying
- Low pure water and energy requirements
- Moderate capital cost
- Simple to automatise

- No lifting of heavy baskets
- Virtually no machine drag-through

Disadvantages

- Unless automated, requires some manpower
- "Footprint" relatively large (up to 6 m^2)
- Peak power consumption high (average low)
- Combustible solvents need module with different concept
- Flammable solvents excluded

2.7.3 "Tank-line" batch types

"Tank-line" types of batch machinery are available for use with some solvents, (including some HCS solvents), some emulsion cleaning and most forms of aqueous cleaning. They are characterised by separate tanks, usually agitated immersion, for each operation, in line. The baskets are usually handled by automatic transfer mechanisms ("hoists") which are designed to perform both the lifting and linear movements.

Advantages

- Some will accept output of soldering machine (5-15 $m^2.h^{-1}$)
- Low pure water requirements
- Simple to automatise
- No lifting of heavy baskets
- Virtually no machine drag-through
- Highly flexible modular conception
- Combustible solvent-compatible

Disadvantages

- Unless automated, requires some manpower
- "Footprint" large (up to 12 m^2)
- Cleaning not always as good as may be required
- Drying not always as good as may be required
- Energy consumption may be high
- High capital cost
- Flammable solvents excluded

2.7.4 Totally enclosed types.

Totally enclosed types of batch machinery are available for use with all solvents, emulsion cleaning and all forms of aqueous cleaning. They are characterised by a sealed cleaning chamber and tanks containing the various liquids which can be pumped in and out the chamber.

Advantages

- Lends itself to rotary agitation
- Lends itself centrifugal drying
- Good cleaning quality possible
- Good drying quality possible
- Small footprint possible
- Excellent flexibility

- Vacuum drying after centrifugation
- Easy inert atmosphere purging
- Combustible/flammable solvent-compatible

Disadvantages

- Assembly size and weight may be limited
- Very small throughput (typ. 1-2 $m^2.h^{-1}$)
- High capital cost
- Long cycle times
- High machine drag-through

2.7.5 Conveyorised "in-line" machines

Conveyorised "in-line" types of machinery are available for use with all solvents, emulsion cleaning and all forms of aqueous cleaning. They are characterised by the form of a tunnel divided into compartments for each function and through which an open mesh conveyor belt transports the assemblies for cleaning. *Warning: there are some smaller conveyorised machines available which do not comply with all the criteria listed below and which are often inefficient in terms of cleaning and/or drying quality.*

Advantages

- Can be matched to any machine(s) for throughput capacity
- Virtually no manual production operations
- Modular types flexible
- Easy handling of combustible solvents
- Inert gas purging possible for flammable solvents

Disadvantages

- High to very high capital cost
- Large to very large footprint
- High production rates impose very long machines (>15 m)
- High energy and pure solvent water demands
- Generally poorer cleaning quality than batch machines[10]
- Generally poorer drying quality than some batch machines[10]
- High drag-out on horizontal assemblies
- Angle of spray attack usually less than ideal

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[10] These generalisations should be qualified by the statement that a few, costly, state-of-the-art machines may give excellent cleaning and drying results. They are based on the fact that if a conveyor moves at 1.5 $m.min^{-1}$ and a cleaning, rinsing or drying phase of the process requires, say, 2-3 minutes to achieve good results, the compartment for that phase should be 3-4.5 m long and be equipped with the appropriate treatment for the whole of that length. Few machines offer this possibility. Slowing down the conveyor may dramatically improve this situation but at the cost of perhaps not being able to use the other machinery to full capacity.

2.7.6 Vapour phase solvent machines

These can be used only with solvents whose boiling point is sufficiently low so that the parts being cleaned are able to support the temperature and whose vapour is much denser than air. The components must also be compatible with the solvents and their vapours (please consult the manufacturers' literature). Halocarbon solvents were most often used with this technique.

As awareness of environmental problems increased, such machines became more sophisticated with features to reduce emissions. Nevertheless, few of the open-top batch machines are able to reduce emissions to acceptable levels when using CFCs, HCFCs, HFCs or PFCs. On the other hand, some of the fully enclosed, entirely automatic ones may be acceptable. Their use with less polluting solvents is not so critical but it is still a wise economical and environmental precaution not to permit any emission that is not strictly necessary. For this reason alone, open-top vapour phase solvent machines are undesirable for use with any solvent used for defluxing or drying printed circuit assemblies.

There is a problem when using any solvent in vapour phase in conjunction with PCB assemblies, especially for tightly packed surface-mounted ones, regardless of the machine's design. Vapour becomes trapped under the components and, as the assemblies are removed from the vapour zone, it takes considerable time for the trapped vapour to fall back into the machine, often counted over several minutes. The machine design and programming must take this factor into account.

2.8 MACHINE AGITATION

The efficiency of a cleaning operation is often a critical function of the method and total energy used in agitating the solvent with respect to the parts being cleaned. This reaches a peak when cleaning under large surface-mount devices with small stand-offs from the printed circuit. This section gives a brief discussion of the most usual types encountered.

2.8.1 Sprays for cleaning

Spray cleaning, correctly applied, is the most efficient way to remove soils. The function is to ensure a maximum high-energy penetration of the fluid into all the crevices, over the required time. Many cleaning processes may require several minutes to ensure dissolution of the soils, even with high-energy spraying.

The form of the sprays should be solid, coherent jets or linear curtains applied to the parts at an acute angle. This angle should be as small as possible to ensure minimum loss of kinetic energy by the fluid "puddling" on the substrate, but should not be so small that severe shadowing occurs. Empirical tests reveal that the best compromise, depending on the machine design, is usually 15° to 45° with respect to the substrate surface. Batch machines are generally better than conveyorised machines in this respect. The geometry of the spraying should be such that all parts of the board are subjected to direct jet action at least over a part of the cleaning cycle. This implies that there should generally be relative movement between the nozzles and the assembly in both axes.

The efficiency of spray cleaning is dependent on the kinetic energy with which the cleaning fluid is sprayed onto the assembly. This is a function of the spray pressure, the spray volume, the fluid velocity, the nozzle design, the distance between the nozzles and the assembly and some minor factors. It is perhaps important to note that a given energy may be imparted equally by a high pressure, low volume or by a low pressure, high volume flow, but the nozzle design would be different in each case. The energy is given by the pump and if a pump consumes a given power at the same efficiency, the results will be similar, no matter what the pressure and volume, assuming correct jet design. As a rule of thumb, for reasonably efficient cleaning of electronics assemblies, the minimum practical energy level of a jet bar is approximately represented by 2 kW (2HP) of pump motor consumption per total metre length of bar.

The high energy levels produced by efficient spray cleaning are partially dissipated when the jets or curtains hit the assemblies. As a rule, the higher the velocity, the more is the energy lost by the rebounding of the solvent from the topography of a typical assembly. This often produces a fine mist. Even with combustible liquids with a flash point of 100°C or more, this mist can be easily ignitable and, if the proportions are right, even explosive. It is therefore essential to correctly inert-gas purge any machines where spraying of flammable or combustible fluids occurs and to use flame-proof and/or inherently safe electrics and electronics in appropriate premises.

The removal of HCS solvents by water is a cleaning operation and not a rinsing one: it must be followed by a rinsing operation.

2.8.2 Sprays for rinsing

The whole function of rinsing is different from cleaning and efficient rinsing is best achieved by low-energy spraying. It should be remembered that at least the last rinse or rinses should be done with pure uncontaminated solvent or water, so the volume consumed should also be minimised. The function of rinsing is to replace the contaminated solvent or water by successive amounts of a cleaner product of the same nature. In other words, it is a series of successive dilutions until the residual contamination level is acceptable.

The best spray form is a coarse mist with a mean droplet size smaller than the smallest interstice, so that there is direct penetration with displacement of the contaminated fluid before much mixing occurs. It is therefore inefficient to use energy levels which are too high. A typical pump energy level for good operation is 200-500 $W.m^{-1}$ of spray bar and the nozzle design should be such that the spray velocity is low with a droplet size of typically 20-100 μm. This may be achieved most efficiently with pressures of about 3 bars.

Again, the angle of attack should be acute at the moment of impact. This may imply almost horizontal nozzles on conveyorised machines, if the velocity is fairly low, as recommended above. Batch machines, with the assemblies held in baskets in a near-vertical position, offer the best and most economical rinse conditions, but the nozzle design may require to be different for the top and bottom spray bars, due to the effect of gravity.

Machines which use the same spray bars for cleaning and rinsing are essentially a compromise in that neither operation can be done under optimum conditions. This may be partially compensated for by adjusting the cleaning and rinsing times and the number of rinses. One severe disadvantage of such machines is the "drag-through" caused by contaminated liquid from the previous operation remaining in the pipe-work, so that clean rinse liquid is contaminated even before it reaches the assemblies being cleaned. This can severely compromise the throughput and liquid consumption of such machines by increasing the number of rinses before adequate cleaning quality is achieved.

2.8.3 "Under-surface" spraying

"Under-surface" spraying is not new, but it has regained popularity as a means of mechanically agitating combustible solvents without forming an ignitable mist. It consists of high-energy jet spraying of the parts being cleaned with the said parts actually immersed in the liquid. The hydrodynamics of the spraying is complex and the kinetic energy loss is high over relatively short distances. As the boards are usually held vertically in a basket or jig (batch machines) or at a 30°-45° angle on conveyorised machines, the jets are most frequently applied edge-on or close thereto. To calculate the required pump size, count on at least 5 HP for each square metre of area being agitated, plus an extra 10% for each 10 cm of the distance over which the jets should remain effective (rule of thumb). In this case, in order to keep the jets as coherent as possible over a distance, it is essential that the pressure be high (>20 bars) and the volume low.

The high kinetic energy is dissipated thermally within the solvent. It is possible that the temperature rise may reach bounds where it approaches the fluid flash point. In this case, water cooling will be necessary. The working temperature should always be maintained at 20°C under the flash point with additional safety devices to shut the machine down completely at 15°C under the flash point.

There is no advantage to using this technique over conventional spraying with non-flammable substances and its poor energy efficiency is marked.

2.8.4 Ultrasonic agitation

The use of ultrasonics on electronics assemblies is the least understood and most controversial cleaning technology.

The main classes of components reported as being potentially damaged by ultrasonic agitation are non-moulded semiconductors (metal, glass and ceramic cases), thermionic devices, large multilayer ceramic chip capacitors, liquid crystal displays and components wound with unencapsulated fine wires. This list is probably not exhaustive and it certainly does not mean that all components of the mentioned types will fail after ultrasonic cleaning. It means that particular prudence is required when judging whether assemblies with any of these components on may be cleaned or not.

Most experience with ultrasonic cleaning was with CFC-113. *It is of first importance to note that data obtained with one solvent type should never be considered as necessarily valid with a different solvent type.* The compressibility and cavitational characteristics of any liquid is unique to that liquid alone.

The first essential criterion to effective ultrasonic cleaning is for cavitation to occur on the surface to be cleaned. This condition can be achieved only if there are no dissolved gases and no particles between the transducers and the parts, otherwise all the ultrasonic energy will be dissipated away from the cleaning zone, where it will serve no useful purpose. To achieve adequate cavitation in water or aqueous solutions, for example, they must be degassed two or three times a day and continually filtered down to 1 μm particle size. Degassing is usually done by subjecting the solution under mechanical agitation to a moderately high vacuum (<1 mb) at 30-50°C. Some organic solvents can never be degassed sufficiently to achieve good cavitation. The quality of emulsions can also vary by the application of ultrasound.

Frequency is another cause of misunderstanding. Ultrasonic energy is created by the instantaneous implosion of cavities and the consequent adiabatic compression of vapour therein. This causes an astronomic rise of temperature to thousands of degrees over an extremely short time, measured in nanoseconds, in turn causing a mechanical shock wave to form in the virtually incompressible fluid. This shock wave does the work. It is typically amortised within a millimetre of the point of cavitation, hence the importance of cavitation on the part being cleaned, preferably on the contaminant itself. Cavities do not form at the frequency of the ultrasonic energy but build up slowly over tens or even hundreds of cycles. This slow rise is a means of storing energy which is released at the instant of implosion. The high-energy shock wave is therefore completely aperiodic and cannot be the cause of a sustained resonance. On the other hand, if there are undamped or poorly damped mechanically resonant parts, such as unsupported wires or quartz crystals, these may be set to oscillate instantaneously at their own natural frequency, no matter what this is. Repeated oscillation may cause, in the long term, fatigue which could lead to a loss of reliability. For the ultrasonic energy to cause direct damage by resonance to a part would seem highly improbable. The following conditions would have to be united:

- the resonant part would have to have a natural frequency exactly equal to the excitation frequency
- the resonant part would have to have a high Q to obtain sufficient amplitude to cause fatigue
- the excitation frequency would have to be stable, which is rarely the case
- the excitation would have to be unmodulated to maintain continuous oscillation, which is rarely the case
- the direction of excitation would have to be such that the amplitude of oscillation was maximised.

It is unlikely that all these conditions would apply. Frequency seems, therefore, not to play a direct role. On the other hand, it can play an indirect role in that lower frequencies may produce larger but fewer cavities, so that the implosion energy per cavity may be greater. Some systems use sweeping frequencies. Over narrow bands (up to one octave), this technique would not bring about any significant difference. Another new technique, developed in Japan, is to use simultaneously three frequencies, such as 35 kHz, 70 kHz and 200 kHz. It is claimed that this is particularly effective, with correct dosing of each of the three amplitudes, when using degassed water or aqueous solutions.

No matter what system is employed, successful use of ultrasonic cleaning depends on:

- cavitation occurring in close proximity to the contaminants
- cavitation of sufficient amplitude/frequency characteristics to ensure adequate acceleration of the cleaning process
- thoroughly degassed solvents or solutions
- very tight process control
- provably, no deterioration of components
- provably, a *significant* improvement in the residual contamination levels

If any one of these criteria cannot be met, ultrasonic cleaning should not be used. In the last condition, "significant" means that if the levels are not at least 30-50% lower than without ultrasonic cleaning, under otherwise identical conditions, then the process is not optimised.

2.9 DRYING

Drying is an important part of the cleaning process and can contribute to the overall success or otherwise of the operation. The most common methods of drying organic solvents and water fall into three categories, mechanical drying, evaporative drying and vapour phase drying. Each of these has a number of sub-categories.

Whether an organic solvent or water (or a mixture in some cases) is used as the final rinse, it must be realised that drying does involve thermal considerations by all three categories enumerated above.

2.9.1 Mechanical drying

The two main subcategories of mechanical drying are effective air-knifing and centrifugation. In both cases, they are accompanied, to a certain extent, by a small proportion of evaporation. This absorbs sufficient heat from the ambience to provide the required latent heat of evaporation. The result is a drop in temperature. With some organic solvents, this may be sufficient under some conditions to take it below the dew point, causing condensation of atmospheric humidity onto the assemblies and subsequent further difficulties. The latent heat of condensation of this water will supply some of the heat required to evaporate the solvent and an equilibrium will be reached (assuming the solvent is not water soluble). It is sufficient to ensure that the air in the knife or in the centrifuge, along with the assemblies, is a few degrees higher than the ambient temperature to avoid this. In any case, the compression of the air in the air-knife system should be sufficient to ensure an adequate heat input.

Mechanical drying is, by far, the most effective means of gross drying. Ninety to ninety-five percent of residual water can be eliminated from even tightly packed surface-mounted assemblies in a matter of thirty seconds. This will require less than 10 percent of the energy needed to evaporate an equivalent mass of water. High-boiling point solvents, e.g. diglycol ethers with boiling points in excess of 200°C, are much more recalcitrant to mechanical removal. This is because their evaporation rate is insignificant below 100°C but, above all, they wet the substrate and components better in the interstices, making them more difficult to shift. In some recorded experiments using hot air-knives at 80°C, on circuits with a medium-high density of SM components, water was retained at an average of 4.2 $g.dm^{-2}$ after immersion in water followed by ordinary handling. Dipping into a solvent with a boiling point of 210°C, the average weight of retained solvent was 3.9 $g.dm^{-2}$. After 20 seconds air-knifing at 80°C, the figures were respectively 0.5 and 1.8 $g.dm^{-2}$. After five minutes, the residues were <0.01 (the limit of measurement, approximating to total dryness) and 0.55 $g.dm^{-2}$ respectively. Even after 30 minutes, the solvent-wetted boards were not dry, even with the combination of high-velocity air and moderately high temperature. Repeating the experiment with water to which 5% of isopropanol was added changed the mean zero and 20 second weights to 4.05 and 0.35 $g.dm^{-2}$ respectively, a distinct improvement over water alone. (These figures were derived from experiments conducted in 1993 by a Swiss company which requested anonymity.)

The supreme advantage of mechanical drying is that most of the water or solvent is eliminated in discrete droplets, typically 100 μm - 1 mm diameter. As seen earlier, rinsing is a process of successive dilutions. There are therefore always some contaminants in the residual liquid and these are eliminated along with the droplets. This method therefore produces a significant improvement of cleaning quality over other methods of drying.

There is no evidence of an increase of fire risk when hot-air knifing combustible solvents. The droplet size is large and the air velocity is high, so that the concentration cannot reach dangerous levels, provided that the air temperature is kept well below the flash point (at least 20°C less).

It may perhaps be useful to define air-knifing in this context as some machine manufacturers mistakenly call forced-air circulation air-knifing. With an air-knife, there are two criteria: the air is forced through a linear orifice, usually a few millimetres wide, and impinges directly onto the parts to be dried. The air velocity is generally about 50 $m.sec^{-1}$ or more. In in-line machines, two or three air-knives on each side provide the action.

2.9.2 Evaporative drying

This consists of either letting the residual liquid evaporate to dryness or to force it dry by increasing the temperature and/or reducing the pressure. The usual means for this are heating by convection, forced air, Infra-red radiation in ovens or tunnels or vacuum ovens.

The chief disadvantage of evaporative drying is that, as drying progresses, the volume of liquid diminishes. The remaining liquid tends to move to where the capillary spaces are smallest, as the contaminants become gradually more concentrated in it. These spaces are mainly round the solder joints. Eventually, these contaminants will become dry at the places where they are deposited, often where they can cause the most electrical or chemical harm. It is for this reason that it is stated above that mechanical drying is preferable for the gross liquid removal. Evaporative drying is used for the remaining 5 or 10 percent that mechanical drying will not remove.

One of the important aspects of evaporative drying is the large amount of power required to supply the latent heat of evaporation of the liquid being removed. In the case of water, for example, about 6.5 kWh is required to dry off each litre of water at 80°C, assuming a 10% heat transfer efficiency (typical for a forced air oven, convection ovens being even less efficient). This is typically ten times higher than is required for mechanical removal. This is another major reason why the latter is preferable for gross drying. Vacuum drying does not escape this rule, even though it is achieved faster and at a lower temperature. Any power gained by not heating the solvent to such a high temperature to obtain a suitable rate of evaporation is more than compensated for by the power consumed by the vacuum pump itself. The latent heat of evaporation remains substantially constant over a wide temperature range and this represents the major part of the power requirements.

Vacuum ovens must be fitted with effective vapour traps to prevent water or solvent vapours from entering the pump, causing a deterioration of the lubrication and thus damage and to prevent lubricating oil vapours from refluxing into the oven, where it could condense in the oven and onto the workpieces.

Infra-red drying efficiency depends on the absorption characteristics at the wavelength of the radiation source. Black and other dark components tend to become hotter than the relatively light ones and the substrate. This temperature differential may become relatively great in some cases.

Forced air drying is the means for the most uniform heating of wet assemblies.

2.9.3 Vapour phase drying

This is the familiar way of drying after solvent cleaning using CFC-113 or 1,1,1-trichloroethane. There are three variants, all based on the same basic idea. These are drying off a solvent in its own vapour, drying off a solvent in the vapour of another solvent miscible with it and drying off a solvent with another one which is not directly miscible with it.

It is important to understand the operating mode of a typical straight vapour phase cleaning operation. The parts to be cleaned are immersed in the boiling solvent for gross cleaning. They are then transferred to a clean, cold solvent bath for rinsing. They should stay there until, at least, the whole assemblies cool to the solvent temperature. They are then lifted out of the liquid into the solvent vapour. Solvent condenses on the parts and gives a final rinse of relatively clean solvent. The latent heat of condensation released causes the parts to heat up rapidly and condensation ceases when they reach the same temperature as the vapour itself. The parts can then be slowly withdrawn slowly out of the machine in such a way as to prevent any vapour from being drawn out with them. This technique is not generally recommended for defluxing because there are many substitute processes which are less polluting and give better results.

It is also possible to dry miscible solvents and recover the drag-out by using vapour phase drying. This is theoretically possible using any solvent which mixes with the cleaning solvent and satisfies the criteria in the previous sections. This is perhaps amongst the most efficient ways to dry off high boiling point solvents (typically BP >170°C and flash point >85°C). This can be done with many solvent families but with all the disadvantages of vapour phase cleaning. In effect, the vapour phase solvent cleans off the contaminated cleaning solvent. In recent years, it has been proposed to use HFCs and PFCs, which are greenhouse gases, for this application. As the emissions of the polluting vapour phase solvents are always more than finite and there are other ways to achieve similar or better results for electronics cleaning and drying, it is not a recommended process.

The Solvents, Coatings and Adhesives Technical Options Committee does not recommend vapour phase drying of heavier solvents using HFCs and PFCs in the electronics industry, under the terms of Multilateral Funding[11].

The use of vapour phase drying of non-miscible solvents is most commonly applied to water. It is exactly the same as the previous case except that there is one intermediate step between the cleaning and drying operations. This involves wetting with some form of third solvent which is miscible or can be made miscible with both the cleaning and drying solvents or displaces the cleaning solvent. One way of doing this, with water as the cleaning solvent, is to use an oxygenated hydrocarbon solvent such as a light alcohol or a heavier diglycol ether. This will dissolve the residual water and the resultant mixture can be dissolved in the drying solvent. Another method is to use an intermediate bath of the same solvent as the drying solvent to which some surfactant is added. To displace water from a part, a light aromatic hydrocarbon may be used, such as toluene (with flammability and toxicity problems to be overcome). Drying water using vapour phase techniques is neither useful nor viable for ordinary electronics assemblies, although it may have applications for some complex optical parts. As it is as polluting as the last process, it is equally not recommended in this context.

The Solvents, Coatings and Adhesives Technical Options Committee does not recommend vapour phase drying of water using HFCs and PFCs in the electronics industry, under the terms of Multilateral Funding[12].

2.10 CONTAMINATION AND QUALITY CONTROL

There are three factors which must be analysed to ensure sufficient quality in relation to the job to which the soldered and possibly cleaned assemblies will be put and to the expected lifetime. These include the following:

- Is the soldering quality sufficient that the rate of retouching is small and that the risk of breakdowns due to faulty soldering is negligible?
- Is there any likelihood of electrical failures due to the presence of contaminants causing corrosion or leakage during the expected lifetime of the assembly under the expected worst conditions of service?

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[11] All vapour phase drying processes emit CFC, HCFC, HFC or PFC vapours. Where these are not already restricted, they may be the subject in the future to restrictive legislation designed to curtail emissions of "global warming gases" which may be a cause of climate change.

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- Is the total process arranged so that the production quality can be constantly monitored and, if necessary, corrected and is it likely to introduce by itself problems which can upset later quality controls as well as in service?

The first two of these questions relate directly to the reliability of the product. The third one is an internal production problem which is not always evident. One simple example is that if a "No-Clean" soldering flux with a high level of residues is used, automatic testing may be upset by contact problems.

As a general rule, the third question is answered by a series of empirical trials. These trials are usually on-going until the whole production line runs smoothly. The first two questions are answered by three forms of instrumentation.

2.10.1 Solderability testers

There are several types of solderability tester available on the market. The most usual one uses the "wetting balance method". There are two variants, using a solder bath and a globule. The first-named is most generally useful for printed circuit boards and wired components whereas the latter type is certainly indicated for surface-mount chip components, but can also be used on some other component types. Some instruments have interchangeable solder sources. All incoming components, including PCBs, should be tested to ensure good solderability and this is especially important with "No-Clean" processes where operating windows are often so narrow that a small reduction of solderability will create catastrophic problems.

2.10.2 Ionic contamination testing

Ionic contaminants are those that are most likely to cause electrical problems in an assembly. With "No-Clean" processes, there is a deliberate introduction of ionic contaminants that is hopefully controlled by the process parameters and thus rendered more-or-less relatively harmless. Ionic contamination testing after such a soldering process is meaningless. On the other hand, it is very important to test incoming components and PCBs with an adequate instrument because any contaminants will pass through the process and produce any one or more of three effects:

- they may upset the soldering process
- they may upset the careful balance of the flux residues, causing poorer electrical quality and corrosion
- they may be the cause of a definitely shorter lifetime of the assembly under service conditions.

This is therefore an essential element of "No-Clean" techniques relating to quality.

Where cleaning is carried out, testing of incoming components may be often dispensed with because the soldering processes are usually more tolerant of minor solderability problems and any incoming contaminants should be at least partially removed during the cleaning process.

When CFC-113 azeotropes were used for cleaning, the process was relatively "fail-safe". This meant that inadequate cleaning often resulted in a slight drop in quality. This is not the case with most substitute methods. Ionic contamination testing is the preferred QC aid to ensure that the quality is maintained at an acceptable level and is a "must" for most users. Low-cost process-control instrumentation is therefore becoming available as well as the very sophisticated testers, which have been available for many years.

2.10.3 Surface insulation resistance and electromigration testing.

SIR testing has been largely ignored as a means of quality control until recently but is often used as a qualification procedure for methods. New variants have contributed to its being adopted as a production test with accelerated test times of about 8 hours. This is aided by the relatively recent introduction of new automated test instruments which take the difficulties out of the practical measurement.

Such SIR test techniques are an extremely good complement to ionic contamination testing, but it is emphasised that each gives part of a total picture with almost no overlap. On occasion, either may indicate dangerous conditions of residual contamination that the other could never even detect.

They are usable after all types of cleaning process *and* after "No-Clean" soldering. They are especially useful after aqueous cleaning methods.

2.11 PHOTORESIST DEVELOPMENT

In the 1991 Solvents TOC Report (UNEP 1991), a detailed section was published on the problems of developing dry film resists used for etch, electroplating and solder masks with 1,1,1-trichloroethane. This is a niche application in the printed circuit manufacturing industry.

Dry film resists were introduced in the late 1960s and they quickly found a ready and wide market for some applications. They were initially all 1,1,1-trichloroethane-developed. They supplanted wet resists for most PCB manufacturing applications. The process caused both considerable OD solvent emissions, as the solvent was sprayed, and water pollution, as there was solvent drag-out into a final water rinse.

By the mid-1970s, aqueous-developed dry-film resists became available. These were slow to become popular as the process was initially more difficult to master and the reject rate was higher. These early problems were overcome and, by 1980, probably over half of the dry film resist used, of all types, was aqueous-developed, with an ever-increasing proportion.

By the mid-1980s, aqueous methods were used for over 90% of etch and plating mask applications and 75% for solder resist applications. The remaining solvent-developed operations were generally reserved for state-of-the-art applications, where the fine-line qualities of aqueous methods were perhaps at the limit of the technique.

Today, there are substitutes available for 1,1,1-trichloroethane-developed dry-film photoresists for all applications:

a. Etch and plating resists:

- aqueous-developed dry film photoimaging resists
- aromatic solvent-developed wet-film photoimaging resists
- aqueous-developed wet-film photoimaging resists
- fine-line silk-screening UV-curing resists
- fine-line silk-screening thermal-curing resists

b. Solder resists:

- aqueous-dev. dry-film photoimaging (not universal)
- curtain-coated HC-developed wet-film photoimaging
- curtain-coated aqueous-developed wet-film photoimaging
- screen-coated HC-developed wet-film photoimaging
- screen-coated aqueous-developed wet-film photoimaging
- fine-line silk-screening UV-curing resists
- fine-line silk-screening thermal-curing resists

For further details and a more technical discussion on this matter, please refer to the 1991 Solvents TOC Report (UNEP, 1991)..

There is no technical nor economic reason why 1,1,1-trichloroethane-developed dry-film photoimageable resists of any nature should continue to be used: there is a wide choice of substitutes suitable for all applications.

2.12 SUMMARY

The electronics industry, which was heavily dependent on ozone-depleting solvents until recently, is fortunate to have a wide range of substitute materials and processes available. There is no technical reason why any company, large or small, in a developed or developing nation, should not be able to move away from such solvents immediately. Economical considerations, reported in previous editions of the Solvents TOC Report (UNEP 1989, 1991), have shown that most substitute processes for this industry are less costly to run and, most often, give improved technical quality. On the other hand, a relatively large capital investment is sometimes required to obtain the required results. This could be an obstacle, especially for small companies manufacturing "hi-tech" electronics. However, even with heavy amortisation costs, most of these processes can be economically and technically viable.

A number of secondary problems have arisen. One of the most important is the fact that most information has been published only in English. English is the most common language in the electronics industry, although it may be poorly understood, especially in developing nations. This is a severe difficulty which can be overcome only by close cooperation between English and non-English speaking experts. "Hands-on" experience is also essential. It may be useful to publish a series of simple pamphlets (say, up to 16 pages) on single subjects written in English by experienced engineers. These could be distributed to developing nations where local engineers could translate them into the local language. Then they could be published and distributed free-of-charge throughout the local industry. The total cost of this could be less than that of a single mistake in equipment or process selection.

To substitute for CFC-113 in defluxing, there is a large choice of processes, equipment and materials commercially available for production units of all sizes. Considerations of economic and technical viabilities under individual conditions may limit the choices. Where there are no technical specifications that require post-solder cleaning, "no-clean" techniques are often the most economical. This technique is recommended where the reliability criteria can be met. Where cleaning is a requirement, the use of water-soluble chemistry has generally proved to be preferable to most of the other processes, although it is not a universal solution. There is an adequate choice of other techniques where neither of these can be applied.

The choice of substitute methods should be subordinate to environmental considerations. Due to their harmful environmental effects, the following processes should not be selected for electronics manufacturing without a very imperative reason, especially as there are usually more benign processes available that will do the same job. *The Solvents, Coating and Adhesives Technical Options Committee does not recommend the following processes in electronics manufacture for funding under the provisions of the Montreal Protocol Multilateral Fund:*

- *HCFC-141b for defluxing printed circuits*
- *Vapour-phase reflow soldering*
- *Vapour-phase drying of heavy organic solvents using PFCs*
- *Vapour-phase drying of water using HFCs or PFCs.*

Another factor which has become evident only in recent years is that the "operating window" of some substitute processes, including "No-Clean" ones, is considerably narrower than that of traditional ones. If the process is not perfectly mastered, this may result in very significantly increased operating costs for rework. One of the parameters which can greatly influence the width of the "operating window" is the design of the assembly being processed. The design itself should be optimised for the process which will be used in the subsequent manufacture. Changing from one process to another may require a re-design. Fortunately, some of the better CAD systems permit this switch very rapidly by simple word processing in text library definitions of the component "footprints" and in the rules file.

Finally, there are no technical obstacles for a complete and rapid phaseout of ozone-depleting solvents in the electronics industry in developing nations, as well as developed ones. In almost every case it is possible to find substitutive processes that result in significant production cost savings, although they may require a considerable capital expenditure. Amortisation of a correctly-chosen investment is typically one to three years but may require longer periods in exceptional cases. In a few cases, there may be increased energy requirements, but the cost of this will be more than offset by other production cost savings.

CHAPTER 3

PRECISION CLEANING APPLICATIONS

3.1. BACKGROUND

Precision cleaning applications are characterized by the high level of cleanliness required to maintain low-clearance or high-reliability components in working order. They are used in a variety of manufacturing industries, such as in aerospace, microelectronics, automotive, and medical. The primary factor that defines the applications where a precision cleaning process is required is high standards for the removal of particulates or organic residue.

There are many types of contaminants that might be required to be removed in a precision cleaning process. These contaminants are generally divided into either particulate contamination or nonparticulate contamination. Particulate contamination is the type of contamination usually resulting from a preceding manufacturing process, such as cutting, drilling, grinding, or buffing of component parts. Nonparticulate contamination is usually composed of organic residue, such as machining oils, waxes, finger print oil, and so forth.

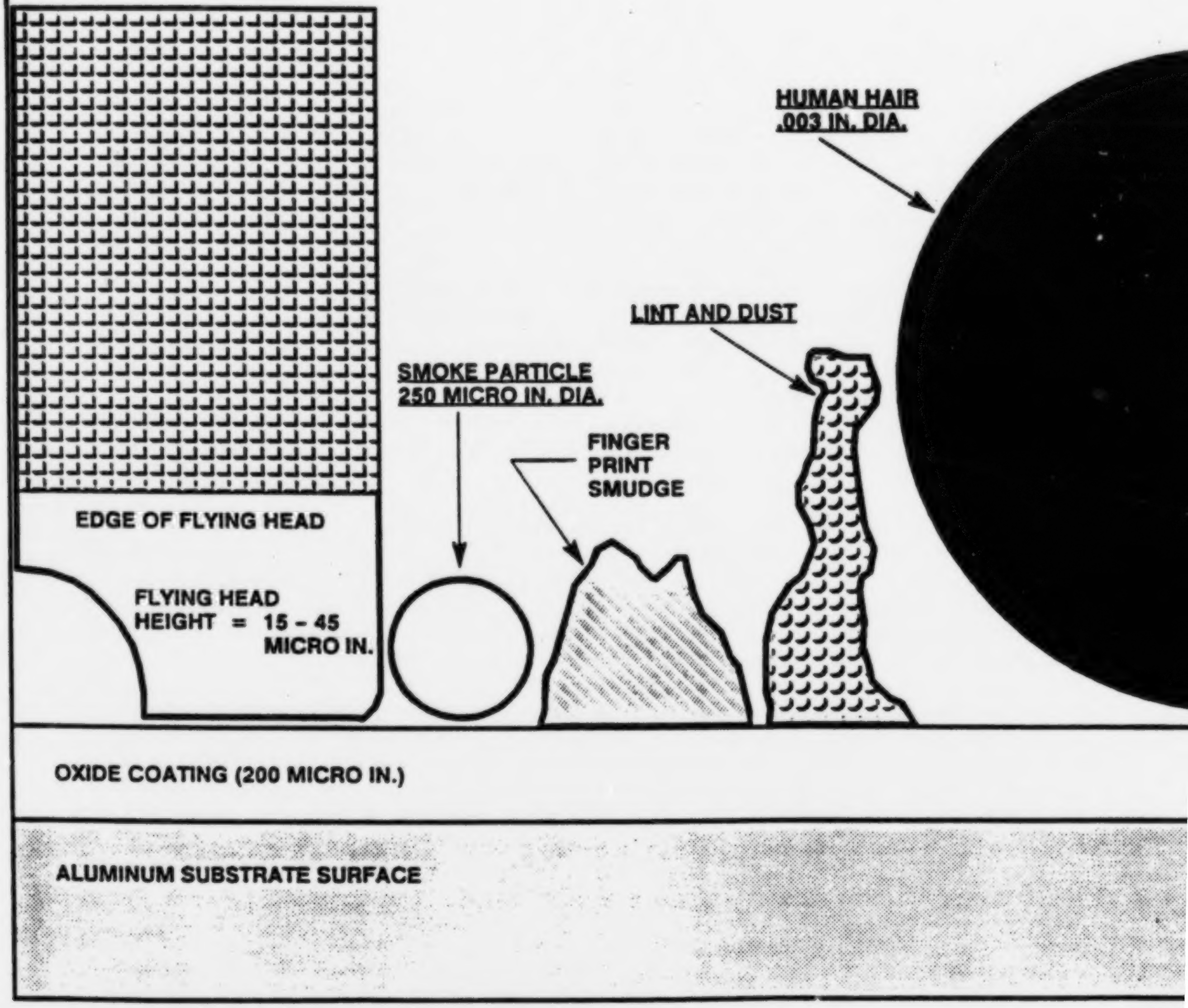
As the term suggests, precision cleaning involves the cleaning of components to a high standard of cleanliness. One example of the cleanliness required for a precision-cleaned component is provided in Figure III-1, which shows the dimensional clearance on a computer disk drive relative to the size of various contaminants. Tight dimensional clearances require the removal of small particles that become lodged between the two surfaces.

The factor that made CFC-113 the precision cleaning solvent of choice is its remarkable chemical stability (manifested directly in its compatibility to structural materials), its low toxicity, and zero flammability. This has allowed closed, superclean, white-room assembly areas to be operated safely and effectively. Probably the most essential example of solvent compatibility is provided by CFC-113 in cleaning beryllium, particularly in the inertial sensor industry. As the performance requirements of gyros increased for both defence and aerospace applications, the need for a structural material that combined low density with high dimensional stability also increased. Hot pressed beryllium has provided that material with a range of properties unique among materials. It has one distinct disadvantage -- chemical reactivity, especially with ionic chlorine. The viability of CFC-113 as a pure, stable solvent has allowed beryllium to be widely used as a structural material. It should be noted, however, that mixtures of CFC-113 with methanol will attack beryllium very vigorously.

1,1,1-Trichloroethane is the solvent of choice in some precision cleaning applications. Several of its physical properties -- higher solvency, moderate evaporation rate, and higher boiling point -- make it a unique product for cleaning some soils, such as heavy grease.

Figure III–1

SIZE COMPARISON OF COMPUTER DISK DRIVE HEAD CLEARANCE WITH VARIOUS CONTAMINANTS


HUMAN HAIR
.003 IN. DIA.
LINT AND DUST
SMOKE PARTICLE
250 MICRO IN. DIA.
FINGER
PRINT
SMUDGE
EDGE OF FLYING HEAD
FLYING HEAD
HEIGHT = 15 - 45
MICRO IN.
OXIDE COATING (200 MICRO IN.)
ALUMINUM SUBSTRATE SURFACE
518028-

Source: Digital Equipment Corporation

518028-1

A number of companies have successfully tested and are currently using CFC-113 and 1,1,1-trichloroethane alternatives to clean precision instruments. Companies also are implementing conservation and recovery practices to reduce solvent use in the short-term. Possible alternatives include solvent and nonsolvent options. Solvent options include aqueous and semi-aqueous, alcohols, perfluorocarbons, synthetic aliphatic hydrocarbons, hydrofluorocarbons (HCFCs) and their blends, and other miscellaneous solvents. Nonsolvent options include supercritical fluid cleaning, UV/Ozone cleaning, pressurized gases, and plasma cleaning. Although much testing still needs to be done for specific applications,[1] the Committee consensus is that alternatives will be substituted for CFC-113 and 1,1,1-trichloroethane in virtually all precision cleaning applications by the year 2000.

3.2 CFC-113 AND 1,1,1-TRICHLOROETHANE USE IN PRECISION CLEANING APPLICATIONS

3.2.1 Precision Cleaning Processes and Equipment

To describe "precision cleaning" in a simple succinct way is difficult. To overcome this difficulty an integrated manufacturing system is described in which the differences in "metal cleaning" and "precision cleaning" become apparent by the nature of the components and the cleaning process.

Figure III-2 shows a diagram containing both metal cleaning (parts manufacturing) and precision cleaning (clean room assembly) processes. In the parts manufacturing segment, parts are manufactured, deburred, gauged, cleaned using 1,1,1 trichloroethane, and stored. In the cleanroom assembly areas, parts and components are passed through a preliminary "goods inwards" cleaning process using CFC-113 and then into final assembly and test. In the final assembly stages, mostly manual, multiple operations are carried out on a given item and the parts are repeatedly cleaned using CFC-113, during and after each assembly stage. When complete the finished item is passed through "acceptance" testing and inspection and then delivered either to detailed functional testing or directly to the customer. Functional rejects, occurring during acceptance testing are often torn-down, recleaned, and returned to the assembly process.

In the first stage, parts manufacturing, single parts will be formed by machining, stamping, pressing, etc. The cleaning requirements include the removal of burrs and other mechanical residues as well as the removal of gross residues of machining oils or other processing residues. In this stage, vapour degreasing with 1,1,1-trichloroethane was a common practice.

Within the clean room assembly area, CFC-113 cleaning would normally follow. Its particular properties of nonflammability, low toxicity, and low odour allow it to be used in small cleaners within laminar flow cabinets or in bench top units close to the operator's working position. Typical devices made in such areas usually contain a wide range of materials. In addition, many items are fixed using synthetic resins, local soldering operations on custom-built hybrid devices are required, and many solvent sensitive polymers

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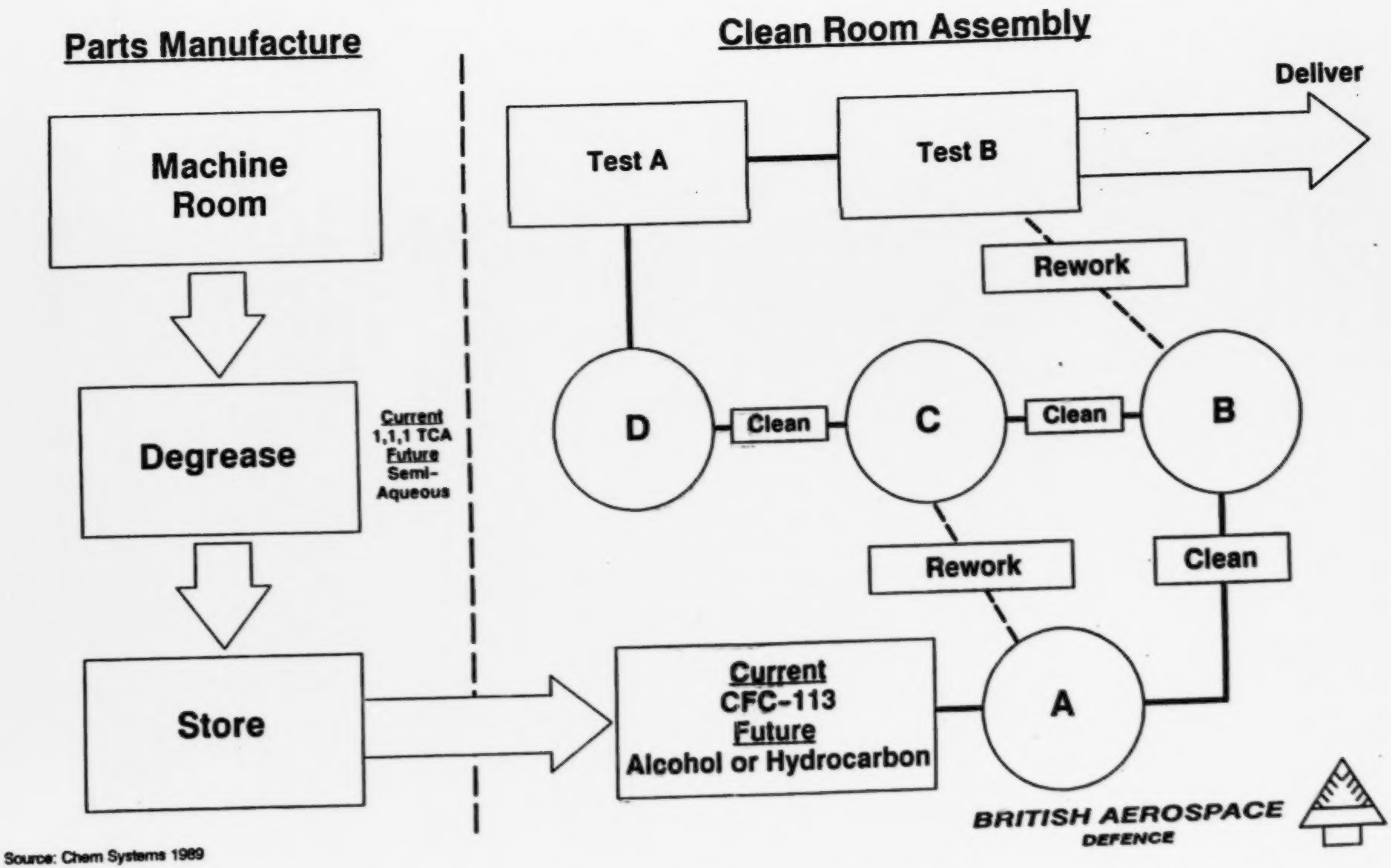
[1] Testing needs to be done not only to determine cleaning effectiveness but cost and environmental effects as well.

Figure III–2

Metal Cleaning and Precision Cleaning


Parts Manufacture
Clean Room Assembly
Machine Room
Degrease
Current
1,1,1 TCA
Future
Semi-Aqueous
Store
Current
CFC-113
Future
Alcohol or Hydrocarbon
A
Rework
Clean
B
Clean
C
Clean
D
Test A
Test B
Rework
Deliver

BRITISH AEROSPACE
DEFENCE

Source: Chem Systems 1989

518028-1

such as polycarbonate and polyether sulphones can be used. The availability of CFC-113 has obviously been vital in such an operation.

Replacement of currently used solvents is relatively easy in the "general cleaning" stage of manufacture. Because the basic components are usually one part items, they can be cleaned very effectively using alternatives such as aqueous and semi-aqueous systems. If this system is incompatible with the parts, due to corrosion sensitivity or shape limitations, then solvents such as alcohols, HCFCs, and hydrocarbons can be used, particularly with closed-type cleaning equipment now available to minimise solvent emissions.

Introducing alternative cleaning materials or processes is particularly difficult in the final assembly precision cleaning area. This is not due to the nature of the soils involved, but due to the wide range of materials used in the manufacture of the assemblies and the small clearances and complexity found in such devices.

Thus precision cleaning applications might include:

- Assembled units with complex shapes and small clearances
- A wide range of metallic and nonmetallic components, including many elastomeric materials
- Blind holes with capillary gaps which make evaporation of low vapour pressure fluids such as water impossible.

Such work pieces are not always small; complete auxiliary power generators and military aircraft generators can be immersion cleaned using CFC-113 during maintenance operations, thus avoiding costly and risky disassembly and reassembly of the units. Alternative cleaning materials or processes, therefore, are required to have low surface tension, low viscosity, and relatively high vapour pressure. Alternative processes must be designed with new cleaning and drying technologies to be used with aqueous and semi-aqueous cleaning systems.

In the past, standard vapour degreasing equipment was used in precision cleaning processes. The equipment is usually comprised of a boiling sump, cooling coils, and a clean rinse stage with ultrasonic generators. These units were often fitted with mechanical handling equipment and installed at the incoming location adjacent to clean areas so that parts, sub-assemblies, and proprietary components could be cleaned and rapidly sealed in bags prior to transfer to the clean room assembly area. Within clean room assembly areas, smaller CFC-113 and 1,1,1-trichloroethane vapour degreasers with ultrasonic generators were often installed close to inspection and assembly areas so that local batch cleaning could be performed.

Bench-top ultrasonic cleaners are used in clean rooms and are often installed within laminar flow boxes. These ultrasonic units are cold cleaners in which water is used as the energy coupling medium. Clean glassware containing a small volume of CFC-113, 1,1,1 trichloroethane, or other nonflammable solvent is placed in the water such that ultrasonic energy can agitate and clean the individual components when they are placed in the solvent. This type of cleaning has a high loss to evaporation; 100 percent of the evaporated solvent is lost to the atmosphere because there are no cooling coils or other forms of vapour containment or collection. Often this technique is combined with particle counting in which all of the solvent is microfiltered after cleaning so that the contaminant particles may be counted under a microscope.

Gyroscope flushing tools are dedicated systems designed specifically for a particular gyroscope. Coupling fixtures attach these tools to the gyroscope shell. Clean CFC-113 is forced through the gyroscope via ultra-filters under pressure in an open-ended process to remove flotation fluid during rework or to clean an assembly before filling it with oil.

Hydraulic system flush and spray booths are similar to gyroscope flushing tools but are larger. The flush mechanism pumps CFC-113 through the hydraulic systems to remove hydraulic fluid. These cleaning machines often have hand-held spray cleaners for manual cleaning of valve seats. Many are 100 percent evaporative systems in which the solvent evaporates and is removed from the work areas by extraction fans. Similar techniques are used in the refrigeration industry to flush out systems before filling.

3.2.2 Precision Cleaning Applications

Precision cleaning is discussed in this report in terms of the following engineering applications: cleaning precision instruments during manufacturing, testing or assembly; cleaning during specialised manufacturing techniques; and maintenance and repair cleaning.

3.2.2.1 Cleaning Precision Instruments During Manufacture, Assembly, and Testing

Precision cleaning is used to remove contaminants from delicate and complex instruments such as computer disk drives, inertial guidance systems (gyroscopes), hydraulic control systems, optical components, and micro-switches. Traditionally, CFC-113 has been effective in precision cleaning the following delicate instruments.

Disk Drives. Disk drives are magnetic storage devices that store information in computer systems. Disk drives have a very small tolerance for contamination during assembly. Normally, the record/read head is spaced from 0.813 to 1.143 microns above the recording media surface of the disk substrate. To place this distance in perspective, smoke particles typically are on the order of 6.3 microns in diameter. Contaminants must be controlled at the submicrometer level for the drives to work effectively (Felty 1991). Possible cleaning alternatives for disk drives include ultrapure water, semi-aqueous processes, and organic solvents.

Gyroscopes. Precision cleaning is used to clean the mechanical components of inertial systems, including gyroscopes and accelerometers.[2] Parts are repeatedly cleaned at all stages of component assembly to remove handling contamination and particulate material. Repeated cleaning is important in gyroscope gimbal assemblies because suspension bearings lubricated with solid film are sensitive to solid particulate contamination. Cleanliness helps to assure torque values of a few microgram (mg) centimetres. To reduce precessional drift, components have often been cleaned in small ultrasonic cleaners using CFC-113.

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[2] Inertial guidance systems or gyroscopes include rate gyroscopes, displacement gyroscopes, and rate-integrating gyroscopes. Displacement gyroscopes typically are used in autopilots. Rate-integrating gyroscopes are used in precise inertial navigation systems in missiles, satellite controls, commercial aircraft, and underwater systems.

In rate-integrating gyroscopes, the flotation fluid surrounding the inner gimbal is a poly (trifluorochloro) ethylene. When the viscosity of the fluid must be changed, secondary fluoropolymers are added. Typically this fluid is poly (1,1-difluoro)ethene. Other fluorinated, high density materials, such as perfluorotrialkylamines, are also used in the assembly and testing stages. A related advantage of CFC-113 is its solubility of these high density polychlororofluoroethylene and polychlorobromoethylene compounds. These compounds are not soluble in common solvents.

Although the floated gyroscope technology is being superseded by solid state, optical systems, commercial and military gyroscope equipment will remain in service for many years. Because these gyroscopes need to be serviced and maintained, there is a long-term requirement for compatible solvents for manufacturing spare sensors and gyroscopes and for cleaning existing units.

Possible cleaning alternatives for gyroscopes include nonozone-depleting chlorinated solvents, organic solvents, hydrofluorocarbons (HFCs), hydrochlorofluorocarbons (HCFCs), aqueous processes, supercritical fluids, and perfluorocarbons (PFCs).

Hydraulic Control Systems. Hydraulic military vehicle control systems have control valves with extremely small diameter bores as well as parts such as O-ring seals and gaskets made of elastomers. These systems are flushed to remove the working fluid and to remove all particulate contamination during assembly, after functional testing, and during field maintenance. CFC-113 has traditionally been the solvent of choice because of its chemical stability and noncorrosive properties. Smaller tactical weapon systems often use a gas control system in which a source of high pressure gas, either chemically generated (e.g., extruded double-based propellent) or a "cold" compressed gas such as nitrogen at 3.56×10^7 N/M^2, controls the actuator systems' valves. Gas controls require extreme cleanliness as they are sensitive to particulate contamination. Gas control systems are pressure tested, and water often is used as the test fluid. Many hot gas control units have long blind holes from which it is difficult to remove water by oven evaporation. Water-displacing mixtures based on CFC-113 effectively dry these systems.

Possible alternatives for hydraulic control system cleaning include alcohols, supercritical fluids, and gas plasma.

Optical Components. CFC-113 solvent and alcohol azeotrope or surfactant solvents along with 1,1,1-trichloroethane are widely used in cleaning and fixturing processes during grinding and polishing operations and prior to applying vapour deposition coatings in optics fabrication. The surface cleanliness of glass and metal optical elements are critical to ensure adequate adhesion of optical coatings and freedom of movement in low torque pivots with small clearances.

Solvent cleaning has been an integral part of the manufacturing cycle for optical components. Solvents used included 1,1,1-trichloroethane, trichloroethylene, CFC-113, CFC-113 with the azeotropes of methylene chloride, acetone, methanol, ethanol and CFC-113 dispersions with water and surfactants as well as individual solvents as methylene chloride, acetone and methyl, ethyl, and isopropyl alcohols. Historically solvents have been the preferred method due to their speed of soil removal, known material compatibility, lack of residual contamination, ease of use, and low cost. Regulatory changes in purchase and disposal of these materials is dictating a change to alternative cleaning techniques. These changes will not be without their associated problems.

Typical part holding (blocking) techniques are used during precision optical grinding and polishing operations utilizing rosin and paraffin-based waxes, pitches, and some cyanoacrylate adhesives. In particular, the waxes and pitches are used for their ability to conform and hold to a variety of irregular shapes and surface textures. The blocking technique involves heating the part and tooling, applying a layer of wax to the tool surface, installing the part, and then allowing the tool to cool before subsequent processing. The waxes and pitches are also nonreactive with water-based coolants and slurries used during the grinding and polishing of optical elements. Cyanoacrylate adhesives are used during a limited number of operations where precision tolerances are required, but are limited by their ability to withstand the dynamic loading and shocks encountered during some of the manufacturing procedures.

After processing, part removal is similar to the blocking technique. The tool is heated, the blocking wax or pitch softens or melts, the part is removed and both part and tool are cleaned. The use of a solvent vapour degreaser allows streamlining of the cleaning sequence since all operations can be performed in a single machine. When the parts/tools are removed from the degreasing operation, they are clean and ready for additional processing steps such as vapour deposition of specialized coatings.

The use of cyanoacrylates as blocking agents requires some form of solvent cleaning to remove all residues prior to additional processing. Much of this cleaning is performed in soak hoods where the contaminated optical element is immersed in solvent or where direct manual cleaning is employed using acetone. Other processing techniques that are dependent on the use of solvent cleaning are the application of protective coatings used during fabrication operations to protect finished surfaces. The current selection of coatings used are solvent based and are resistant to water, again a requirement due to the use of water-based coolant and processing fluids.

Some water-based cleaning is currently in use for rough cleaning operations prior to final, fine cleaning operations. Problems have been noted with residues left after using water-based cleaners prior to vapour deposition thin film coating operations. The negative impact of these residues on the adhesive strength of thin film coatings deposited after such operations has prevented their use in final, fine, or finish cleaning procedures. The reduced adhesion and increased propensity for peeling of the coating is particularly noticeable when completed optical elements are exposed to elevated temperature and humidity conditions.

Water-based cleaners also suffer from material compatibility problems. There are well over 100 types of visible glass and infrared materials (germanium metal, etc.) used in precision optical elements. The need for precise process control, minimization of staining on optics, difficulties with rinsing and drying (formerly used chlorofluorocarbons (CFCs)), and equipment reliability problems associated with utilization of aqueous cleaners have forced manufacturing in many instances to return to manual final cleaning/drying operations utilizing acetone and alcohol solvents to replace CFCs.

The change from solvent cleaning to alternative methods will require significant process changes in the future to completely remove CFCs and 1,1,1-trichloroethane from the precision optics manufacturing process. Blocking materials, protective coatings, and techniques for final cleaning before coating will require change. Material compatibility, cleanliness, and process stability will be critical considerations for any replacement cleaning solvent.

HCFCs may provide an alternative for final cleaning operations after wax and other blocking and grinding/polishing residues have been removed. Testing (Schaefer and Scott 1991) has indicated that the three-carbon HCFC-225 solvent is equivalent to CFC-113 in its ability to provide final cleaning before and after vapour deposition coating operations without introducing stains due to solvent evaporation. Cleaning equipment used for CFC-113 can also be used for HCFC-225 because the boiling point is slightly higher than CFC-113. It is important to operate the equipment, however, with a recovery system to minimize solvent emissions (Yamabe 1991).[3] Newly designed, closed-type equipment is also available to reduce solvent emissions. Initial testing has shown the HCFC-225 to exhibit very poor solubility with the typical blocking waxes and pitches used in the optics manufacturing operation; solvent blends and new soluble blocking materials are being developed to overcome this difficulty. In order to use HCFCs throughout the fabrication cycle, new compatible (soluble) blocking materials will have to be developed.

Recently, manufacturers of glass-based optical elements have shifted away from CFC-113 cleaning solvents. The use of chemically inert CFC-113 solvents is critical for metal-based optical elements such as highly polished or diamond turned (machined) aluminum reflective elements. The highly sensitive metal surfaces are extremely reactive in a fresh, nonoxidised state, and cleaning with substitute chlorinated solvents would detrimentally affect the metal. HCFC-225 has also been evaluated as replacement for CFC-113 (in part due to similar boiling points) in this operation and found to be compatible with the freshly machined surface and capable of final cleaning of such surfaces without generating stains during solvent flash-off.

Other alternatives, known as hydrofluorocarbons (HFCs) and perfluorocarbons (PFCs), have been developed for use in the precision cleaning of optics as well. PFCs are currently commercially available, and HFCs are expected to be available commercially in the next one to two years. Both HFCs and PFCs exhibit low reactivity, vapour pressures similar to that of CFC-113, and relative nonflammability. PFCs have been used for many years as insulating and drying fluids, although the use of PFCs in emissive applications such as solvent cleaning is limited. Both HFCs and PFCs, which do not contribute to stratospheric ozone depletion or to the formation of tropospheric ozone (smog), have been identified as global warming compounds. PFCs are more potent global warmers than HFCs because their atmospheric lifetimes are significantly longer than those for HFCs. Newly designed equipment is available to aid potential users of either PFCs or HFCs. The new equipment is vapour-tight and usually includes options for solvent filtration and recycling within the unit.

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[3] HCFC-225ca and cb have been registered in EINECS, Toxic Substances Control Act (USA) and in Japan.

Gas plasma cleaning has become more popular in the mid-1990's for general precision cleaning of organic contaminants based on the use of the technology developed in the electronics industry in the 1980's. Gas plasma cleaning requires the use of oxygen, carbon tetrafluoride/oxygen, or other gases, to remove trace amounts of organic material. The gas plasma is created when normal gases are excited above their normal energy levels. The excitation of the gases results in the creation of excited oxygen molecules, which then react and oxidize organic molecules to form carbon dioxide and water vapour. Gas plasma cleaning will damage all amorphous carbon-based materials and therefore should not be used with components containing plastics. This type of cleaning finds its way into all of the cracks and crevices of a particular component and is ultimately removed by creating a vacuum on the cleaning chamber. Waste disposal is generally not a concern with gas plasma cleaning as the waste components are only the small amounts of contamination or dirt collected in the gas plasma air filter.

Pressurised CFC-113 is also used for cleaning dust and particles from high definition cathode ray tube shadow works and electron guns. CFC-113 solvent is very efficient as the high specific gravity allows nonmetallic particles to be floated off precision parts (Nemoto 1989).

In the past, CFC-113 was used in many drying operations to prevent streaking and water spot deposition on pre- and post-coated optical element surfaces. Many of these applications, however, have been replaced with high vapour pressure organic solvents. In such applications, since these materials are considered volatile organic compounds (VOCs), vapour retention is critical to prevent the emission of solvent vapours to the atmosphere.

Possible alternatives for optical component cleaning include supercritical fluids, high-purity alcohols, HCFCs, and PFCs.

Electrical Contacts. Micro-switches used for critical switching functions require extremely clean contacting surfaces. CFC-113 often is used to clean these surfaces. The switches also can be cleaned using CFC-113 after assembly to remove particles or oily material deposited during assembly.

Most electrical contacts in connectors, slip-rings, potentiometers, microswitches, and relays have precious metal contacts such as gold, gold alloys, and platinum metals. Precious metal contacts are used in the defence industry where "single shot" devices require a long storage life (up to 15 years) and must operate with greater than 99 percent reliability. High surface contact resistance is a problem as many of these devices are closed "cold" (i.e., without an applied voltage) because of safety requirements. In the past these specifications were met by CFC-113 cleaning. CFC-113 also was used to clean sliding contacts such as slip rings and potentiometers.

Possible alternatives for electrical contact cleaning include supercritical fluids, gas plasma, HCFCs, high purity organics, and nonozone-depleting chlorinated solvents.

Medical Equipment Applications. The small blind holes increasingly found on complex surgical equipment have made it difficult to remove the water from this equipment.[4] A majority of surgical instruments were first dried using CFC-113 water-displacing materials and then were sterilised. Orthopaedic prostheses such as hip joints and knee joints are cleaned and dried using a similar process. CFC-113 was also used to clean pipe-runs, bedside control systems, and main control panel equipment after installation and during maintenance cleaning of hospital piped-oxygen systems. HCFCs and PFCs can now be used to clean and sterilize these systems. The high volatility and nonflammability of CFC-113, HCFCs, and PFCs allows the flushing solvent to be blown through the oxygen system without risk of explosion. Vacuum drying can be used to eliminate any risks of leaving trace amounts of solvent. The chemical stability of CFC-113, HCFCs, and PFCs and the absence of stabiliser chemicals helps ensure that organic contaminants can be removed from the metal parts of the oxygen systems without risk of corrosion.

Possible alternatives for the cleaning of medical equipment include supercritical fluids, gas plasma, high-purity alcohols, HCFCs, PFCs, organic solvents, and vacuum drying.

Plastic Assemblies. CFC-113 was used to remove mould release agents from a variety of plastic mouldings such as ABS electronic cabinet mouldings, domestic white goods accessories, medical parts, syringes, spoons, bottles, and sample vials. The advantage of using CFC-113 in this application is that there is no risk of surface attack or "crazing," which could occur if other solvents are used without considering material compatibility issues.

Possible alternatives in this applications include nonozone-depleting chlorinated solvents and organic solvents where compatible.

3.2.2.2 Specialised Manufacturing Techniques

Precision cleaning also is a component of specialised manufacturing techniques such as auto-rivetting of commercial aircraft wings and precision application of special lubricants. These options are also discussed in further detail in Chapter 9: Other Uses of CFC-113 and 1,1,1-trichloroethane.

Auto-Rivetting. Commercial aircraft wings often are used as fuel tanks. These wings, therefore, must be of minimum weight and maximum strength, have a long corrosion-free life, and be fuel tight. Auto-rivetting is used to meet these requirements.[5] Traditionally, major aircraft companies have used CFC-113 for auto-rivetting because the stock being drilled for commercial aircraft wings is much thicker than that on the wings of fighter aircraft. A proprietary CFC-113 solvent blend is sprayed on the drill tool during cutting and on the rivet slug as it is placed into the bore. Although the rivet slug is anodised, the freshly drilled bore surface is not protected. The solvent spray protects the assembly as it is formed and frees the joint of entrapped moisture or acidic components that might encourage corrosion. The solvent rapidly evaporates and helps cool the form.

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[4] In the past, surgical instruments were dried after washing and then sterilized in hot air ovens.

[5] In this process, the wing skins are clamped to the stringers, a double counter sunk hole is drilled through both components, and an appropriate rivet slug is placed into the bore and the head machined flush with the outer wing surface.

A possible alternative for this application is the use of rivets with dry film lubricants.

Application of Special Lubricants. The surface of miniature precision bearings is coated with a thin oil film. To ensure that the film remains stable over many years of storage life, a lubricant such as a CFC-113 solvent solution is sometimes applied to the bearings. The low surface tension of CFC-113 solvent allows the solution to "wet" the bearing almost instantly. The rapid solvent evaporation leaves a film of oil on the bearing surface. Perfluoroether and cyclopentane-based lubricants, which are used in some space applications due to their extremely low vapour pressure and flat temperature-viscosity curve, use CFC-113 as a carrier for thin film application and to clean bearings as these lubricants are only soluble in a select few organic solvents.

3.2.2.3 Maintenance Cleaning and Repair

Maintenance precision cleaning applications include avionics equipment, glove boxes in the nuclear industry, electronic sensors associated with offshore oil rigs such as remote cameras and well loggers, and reticles used to manufacture semiconductors.

In the past, large commercial airline workshops used large amounts of CFC-113 solvents to clean avionics equipment.[6] In the nuclear power industry, pieces of ancillary equipment that become contaminated with radioactive dusts are removed in glove boxes using remote handling systems. With continued use, the boxes themselves become contaminated. Glove boxes can be decontaminated by spraying with CFC-113 to remove radioactive dusts. The low surface tension and high volatility of CFC-113 provide good wetting and penetration for particle removal. The low flammability and low toxicity of CFC-113 were the main reasons for using CFC-113 on offshore oil rigs where CFC-113 was used to clean sensors such as remote cameras, drill head attitude indicators, and well loggers. Pressurised CFC-113 was used for cleaning dust and particles from reticles used during the manufacture of semiconductors. The reticle is a patterned glass plate through which light is directed on wafers to create circuitry. CFC-113 solvent is very efficient as the high specific gravity allows nonmetallic particles to be floated off reticles (Nemoto 1989).

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[6] Larger aircraft components are cleaned using other chlorinated solvents such as trichloroethylene and perchloroethylene in vapour degreasers and 1,1,1-trichloroethane in cold cleaning and vapour degreasing.

3.3 ALTERNATIVES FOR REDUCING OR REPLACING CFC-113 AND 1,1,1-TRICHLOROETHANE IN PRECISION CLEANING

CFC-113 and 1,1,1-trichloroethane have evolved as the preferred solvent cleaning method in precision cleaning because of their chemical inertness, low toxicity, nonflammability, low surface tension, and low water solubility. However, to eliminate CFC-113 and 1,1,1-trichloroethane use, a number of companies have tested and implemented alternative cleaning methods. Possible alternatives include solvent and nonsolvent options. Solvent options include other organic solvents (such as alcohols and aliphatic hydrocarbons), perfluorocarbons, HCFCs and their blends, and aqueous and semi-aqueous cleaners. Nonsolvent options include supercritical fluid cleaning, UV/Ozone cleaning, pressurized gases, and plasma cleaning. Solvent use may also be reduced by controlled planning of repetitive or multiple cleaning operations. These alternatives are discussed later in this chapter.

Generally, the selection of the most appropriate alternative to either CFC-113 or 1,1,1 trichloroethane should be made based on a number of factors, including technical feasibility, environmental, health, and safety impacts, and cost. Technical feasibility can be predicted by the use of solubility parameter technology, such as Hildebrand parameters. This process is very simple and has proven to be accurate in many cases. The basic process requires the identification of the solute, or contamination, that is to be removed from a particular surface. Next, the solubility parameter of the solute is determined and matched to the solubility parameters of hundreds of common industrial solvents. Several common solvents are selected and the properties of each should be closely reviewed. Finally, one or two solvents can be selected for testing on actual hardware. This is a scientific process on how best to narrow the selection of alternative solvents. For more information on this process, consult "Handbook of Solubility Parameters and Other Cohesion Parameters", Allan F.M. Barton, CRC Press.

3.3.1 Conservation and Recovery Practices

Solvent losses are often large in conventional or poorly maintained plants. In a poorly maintained plant, 20 percent or less of the purchased solvent is generally recovered.

Depending on what measures have already been adopted at a plant, applications of the guidelines summarized in Appendix C can enable total emissions to be reduced by up to 90 percent. Solvent losses can be reduced from 2-5 kg/h-m^2 of bath area with conventional practice to 0.2 - 0.5 kg/h-m^2 of bath area. For certain alcohol and partially aqueous systems, the overall base rate of annual loss is around 0.03 - 0.05 kg/h-m^2 of bath area.

The recommendations summarized in Appendix C can be implemented to reduce solvent use in cold cleaning, vapour degreasing, and continuous in-line cleaning.

3.3.2 Aqueous Cleaning

Aqueous cleaners use water as the primary solvent. Synthetic detergents and surfactants are combined with special additives such as builders, pH buffers, inhibitors, saponifiers, emulsifiers, deflocculants, complexing agents, antifoaming agents, and others. They provide multiple options in formulation blending, such as the use of corrosion inhibitors and pH buffers. Table III-1 summarizes the advantages and disadvantages of aqueous cleaning.

The key stages of an aqueous cleaning process are washing, rinsing, drying, water treatment, and waste recycling/disposal. Although each of these steps in Figure III-3 is an important and integral part of the aqueous cleaning system, rinsing and drying may not be necessary in all circumstances and wastewater disposal may also be integrated into the other steps by recycling bath contents and the overall water use.

Process Equipment

Aqueous cleaning equipment can be characterized as:

- In-line equipment used for high throughput cleaning requirements
- Batch equipment used for low throughput such as for maintenance applications or smaller production processes. The in-line and batch equipment can be further subdivided into immersion, spray, and ultrasonic type equipment. Table III-2 summarizes the advantages and disadvantages of each of these three types of equipment.

Product design can have a significant influence on cleanability. Choice of materials and configuration should be reviewed if possible for opportunities to make changes that can have a major influence on the success of aqueous cleaning. Care should be exercised to prevent trapping cleaning fluid in holes and capillary spaces. Low surface tension cleaning solvent might penetrate spaces and not be easily displaced by the higher surface tension pure water rinse. Penetration into small spaces is a function of surface tension, viscosity, and capillary forces.

Water-based cleaning is a more complex process than CFC-113 and 1,1,1-trichloroethane cleaning. Good engineering and process control are much more critical to prevent problems. Useful parameters for process control include bath temperatures, pH, agitation, rinse water quality, and cleaning bath quality.

Drying presents one of the major challenges to aqueous cleaning for complex parts and may require considerable engineering and experimentation. However, there are some aqueous cleaning systems in operation today in precision cleaning applications that produce spot-free drying. There have been significant changes in the area of spot-free drying over the last several years, and there are commercially available systems that will spot-free dry almost any component.

Aqueous cleaning requires careful consideration of drying. Thermodynamic or evaporative removal of bulk water is usually not practical from the perspective of an energy or process time. Mechanical removal of the water (90 percent or more) can be accomplished in some cases using compact turbine blowers with filtered output. Design options include variation of pressure, angle, velocity, and volume. Other sources of air include dedicated compressors or plant air, but care must be taken to remove oil, particles, and moisture to the level desired. Economics and noise reduction are other considerations in using such options. (Depending on the equipment and plant,

Table III-1

AQUEOUS CLEANING

ADVANTAGES

Aqueous cleaning has several advantages over organic solvent cleaning.

- Safety -- Aqueous systems have few problems with worker safety compared to many solvents. They are not flammable or explosive. Toxicity is low for most formulations, requiring only simple precautions in handling any chemical. It is important, however, to consult the material safety data sheets for information on health, safety, and environment regulation.
- Cleaning -- Aqueous systems can be readily designed to clean particles and films better than solvents.
- Multiple Process Options -- Aqueous systems have multiple process options in process design formulation and concentration. This enables aqueous processes to provide superior cleaning for a wider variety of contamination.
- Inorganic or Polar Soils -- Aqueous cleaning is particularly good for cleaning inorganic or polar materials. For environmental and other reasons, many machine shops are using or converting to water-based lubricants and coolants versus oil-based. These are ideally suited to aqueous chemistry.
- Oil and Grease Removal -- Organic films, oils, and greases can be removed very effectively by aqueous chemistry.
- Multiple Cleaning Mechanism -- Aqueous cleaning functions by several mechanisms rather than just one (solvency), including saponification (chemical reaction), displacement, emulsification, dispersion, and others. Particles are effectively removed by surface activity coupled with the application of energy.
- Ultrasonics Applicability -- Ultrasonics are much more effective in water-based solvents than in CFC-113 solvents.
- Chemical Cost -- Low consumption and inexpensive.

DISADVANTAGES

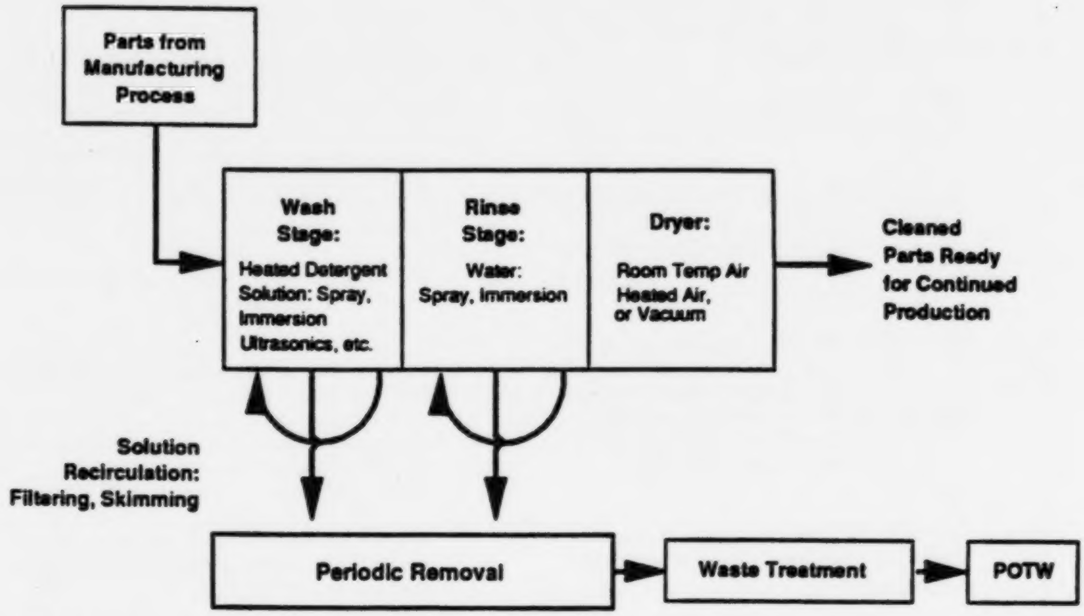
Depending upon the specific cleaning application, however, there are also some disadvantages.

- Cleaning Difficulty -- Parts with blind holes and small crevices may be difficult to clean and may require addition of a vacuum dryer.
- Process Control -- Aqueous processes require careful engineering and control.
- Rinsing -- Some aqueous cleaner residues can be difficult to rinse from surfaces. Nonionic surfactants are especially difficult to rinse. Trace residues may not be appropriate for some applications and materials. Special precautions should be applied for parts requiring subsequent vacuum deposition, liquid oxygen contact, etc. Rinsing can be improved using deionized water or alcohol rinse.
- Floor Space -- In most instances, aqueous cleaning will require more floor space.
- Drying -- For certain part geometries with crevices and blind holes, drying may be difficult to accomplish. An additional drying section may be required.
- Material Compatibility -- Corrosion of metals or delayed environmental stress cracking of certain polymers may occur.
- Water -- In some applications high purity water is needed. Depending on purity and volume, high purity water can be expensive.
- Energy Consumption -- Energy consumption may be higher than solvent cleaning in applications that require heated rinse and drying stages.
- Wastewater Disposal -- In most instances use of aqueous cleaning will require wastewater treatment prior to discharge.
- Water Recycling -- Wastewater may be recycled. Cost of equipment and maintenance can be moderately expensive.

Source: Adapted from ICOLP.

Figure III-3

CONFIGURATION OF A TYPICAL AQUEOUS CLEANING PROCESS


Parts from Manufacturing Process
Wash Stage:
Heated Detergent Solution: Spray, Immersion Ultrasonics, etc.
Rinse Stage:
Water: Spray, Immersion
Dryer:
Room Temp Air Heated Air, or Vacuum
Cleaned Parts Ready for Continued Production
Solution Recirculation: Filtering, Skimming
Periodic Removal
Waste Treatment
POTW

Source: EPA 1989a

Table III-2

AQUEOUS CLEANING PROCESS EQUIPMENT

IMMERSION WITH ULTRASONIC AGITATION	IMMERSION WITH MECHANICAL AGITATION	SPRAY WASHER
ADVANTAGES		
Highest level of cleaning; cleans complex parts/configurations Can be automated Parts can be welded Usable with parts on trays Low maintenance	Usable with parts on trays Will flush out chips Simple to operate Cleans complex parts and configurations Might use existing vapour degreasing equipment with simple engineering changes	High level of cleanliness Inexpensive Will flush out chips Simple to operate High volume Portable Short lead time
DISADVANTAGES		
Highest cost Requires rinse water for some applications Requires new basket design Long lead time Cannot handle heavy oils Limits part size and tank volumes Separate dryer may be required	Requires rinse water for some applications Harder to automate Requires proper part orientation and/or changes while in solution Separate dryer may be required	Requires rinse water for some applications to prevent film residues Not effective in cleaning complex parts Separate dryer may be required

humidity and air-conditioning control as well as associated economics may be an issue.) Centrifugal drying is another useful option for the mechanical removal of water from complex, robust parts. Evaporative drying following mechanical removal can be accomplished using infrared, clean dry air-heated or ambient temperature, or vacuum-heated drying. Dryers can be designed in-line or batch. Drying design should always be confirmed with experimentation.

A very effective means of completely removing water from, or drying, objects with either simple or complex geometries is the use of a vacuum oven. The amount of vacuum and the temperature together with the length of time an object is left within the vacuum oven are variables. They should be matched to the complexity of the object and the nature of its construction (Baxter 1991).

Wastewater minimization and treatment is an important consideration and is discussed in detail later in this report.

Successful cleaning of both disk-drive parts and gyroscope components using aqueous detergent processes has been reported. One major company has switched from a CFC-113 disk drying process to a hot water/air drying system for some applications (Wolf 1988). Aqueous ultrasonic cleaning also has been successfully used to clean inertial guidance and navigation systems and components that are used in some missiles and aircraft in the U.S. Department of Defense inventory (Patterson 1989).

Alternatives to CFC-113 cleaning of inertial systems, gyroscopes, accelerometers, and related gaskets, bearings, and housings include biodegradable aqueous-based systems and nonchlorinated/halogenated hydrocarbons such as alcohols, ketones (acetone), hydrocarbon/surfactant blends, and petroleum distillates. The alternatives may be a combination of systems using ultrasonics, high pressure sprays, surfactants, and ancillary equipment. The following contaminants have been successfully removed using aqueous detergents and ultrasonics:

- A highly fluorinated, long chain polymer lubricant
- Polychlorotrifluoroethylene, a viscous heat transfer fluid with a low coefficient of expansion
- Long chain hydrocarbon oils/grease
- Finger prints
- Inorganic particulate matter
- Rust and other oxides
- Some carbonaceous char.

The cleaning equipment used was a self-contained system that cleans with detergents and water in a cylindrical cleaning tank agitated by ultrasonics. This aqueous system not only has offset use of CFC-113 and 1,1,1-trichloroethane, but has reduced process time as well. For example, while manual cleaning of gimbal rings takes approximately 15 minutes per ring, an aqueous ultrasonic system can clean 24 rings in 25 minutes.

The cleaner provided better cleaning results than those achieved with a solvent-based system. The self-contained system is a promising spray booth media for cleaning parts which cannot be subjected to ultrasonics and also for bench use where spot cleaning is done as part of the repair process.

Nuclear decontamination may be effectively achieved by an aqueous-based system and high pressure sand blasting. Also, Al_2O_3 and/or glass beads of 0.1 mm have been used successfully. In this process, the water evaporates and the residue is cast for disposal (Arvensen 1989).

3.3.3 Semi-Aqueous Cleaning

Hydrocarbon/surfactant cleaners, one type of emulsion cleaner that can substitute for CFC-113 and 1,1,1-trichloroethane in precision cleaning applications, have been included in a number of different cleaners formulated for different purposes. Hydrocarbon/surfactants are used in cleaning processes in two ways: They are either emulsified in water solutions and applied in a manner similar to standard aqueous cleaners or they are applied in concentrated form and then rinsed with water. Because both methods use water in the cleaning process, the hydrocarbon/surfactant process is commonly known as a semi-aqueous process.[7]

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[7] Under certain circumstances, it may be possible to modify an existing single or multi-stage vapour degreaser for use with an alternative solvent. For alternative cold dip cleaners such as hydrocarbons, the vapour degreaser will be used primarily as a containment vessel and the ancillary features such as heaters, etc., are not required. It may also be possible to adapt a multi-stage degreaser for use with the newly emerging semi-aqueous cleaning processes. The details of the conversion procedure will depend on the type of process being considered but the following guidelines illustrate the principles.

A. Semi-Aqueous Processes

Halogenated solvent degreasers are usually fitted with heaters, some form of condensing coils water cooled or refrigerated, safety cut-out devices and in some cases, ultrasonic agitation and/or pumping and spraying equipment.

As halogenated solvents are non-flammable, the equipment designed for their use will have electrical equipment that will not be certified for use in flammable areas. The semi-aqueous processes use flammable fluids. Though the fluids are normally used below the flash point, consideration should be given to a situation where the flash point may be exceeded. In this situation, equipment may have to be modified so that it shuts down in a safe controlled manner.

Process. Semi-aqueous processes consist of one or two immersion stages in the proprietary hydrocarbon formulation followed by rinsing in one or two stages of water. Drying is usually required.

The degreaser should have sufficient compartments to accommodate the chosen semi-aqueous process commensurate with the level of cleanliness required.

Cleaning Stage. The proprietary semi-aqueous cleaner is contained in the first stage(s). Should heating be required then it will need to be determined whether there is sufficient heat input with the existing heating arrangements. Temperatures of 30-50°C are typical, however terpene-based solutions can be used unheated. It may be necessary to include some form of cooling in the event that introduced parts are warm or to counteract excessive heat input from pumps, ultrasonics, etc.

A control system will need to be installed to control the temperature to 20°C below the flash point of the semi-aqueous material. The existing safety cut-out may form part of this system. In addition, a back up system should be fitted which would shut the system down and sound an alarm should the temperature reach 10°C below the flash point of the cleaner.

Rinse Stage. Water can be circulated or agitated with ultrasonics in the remaining stages of the cleaning equipment. It may be necessary to heat the water using the existing heaters to achieve good rinsing and to assist in dry off. There may be significant drag out of the wash liquid into the rinse stages. Water may be re-circulated or passed to drain depending on the process requirements. If the water is to be re-circulated, then appropriate ion exchange or membrane technology may need to be installed to keep the water clean. Similarly, this may be required prior to disposal.

The advice of both the manufacturer of the semi-aqueous cleaning fluid and the degreasing equipment should be sought before attempting such a conversion (Johnson 1991).

B. Alcohol Process

Conversion of standard halogenated solvent degreasing equipment for use with alcohols inerted with perfluorocarbons is not practicable (Johnson 1991). However, some companies have successfully modified

The benefits of semi-aqueous cleaning processes include the following:

- Good cleaning ability (especially for heavy grease, tar, waxes, and hard to remove soils)
- Compatibility with most metals and plastics
- Suppressed vapour pressure (especially if used in emulsified form)
- Nonalkalinity of process prevents etching of metals, thus helping to keep metals out of wastestreams
- Reduced evaporative loss
- Potential decrease in solvent consumption which may lower overall cost
- Ability of some formulas to decant easily from water.
- Lower water consumption as compared to aqueous cleaning

The drawbacks include:

- Recycling or disposal cost of wastewater could make the process less economically viable
- Flammability concerns if concentrated cleaner is used in spray cleaners; however, the flammability issue can be solved with improved equipment design
- Objectionable odours with some cleaners such as terpenes
- VOCs make up some cleaners
- Drying equipment will be required in most applications
- Gelling of some cleaners at low water solutions
- Difficulty in reducing surfactants used in cleaners
- Toxicity considerations not yet established
- Auto-oxidization of some cleaners. For example, d-limonene (a type of terpene) can auto-oxidize. The terpene suffers auto-oxidation naturally from contact with air. This can in some instances be reduced using antioxidant additive
- Semi-aqueous cleaning systems may require more floor space in some instances
- Energy consumption may be higher than that of solvent cleaning systems in applications that require heated rinse and drying stages
- In some applications, high purity water which is expensive may be needed.

The steps in a typical semi-aqueous cleaning process resemble those in aqueous applications. Most equipment designed for use with semi-aqueous processes are also similar to aqueous cleaning equipment designs. Figure III-4 shows the schematic for a typical semi-aqueous cleaning process.

The four major steps used in the cleaning process are washing (with a hydrocarbon/surfactant), rinsing (with water), drying, and wastewater disposal. In cases where extreme cleanliness is required, the hydrocarbon/surfactant cleaning can be followed by a fully aqueous wash step with an alkaline detergent and a deionized water rinse. As in aqueous cleaning, it is important to note that both the wash and the rinse stage are recirculating; these solutions are not continuously discharged.

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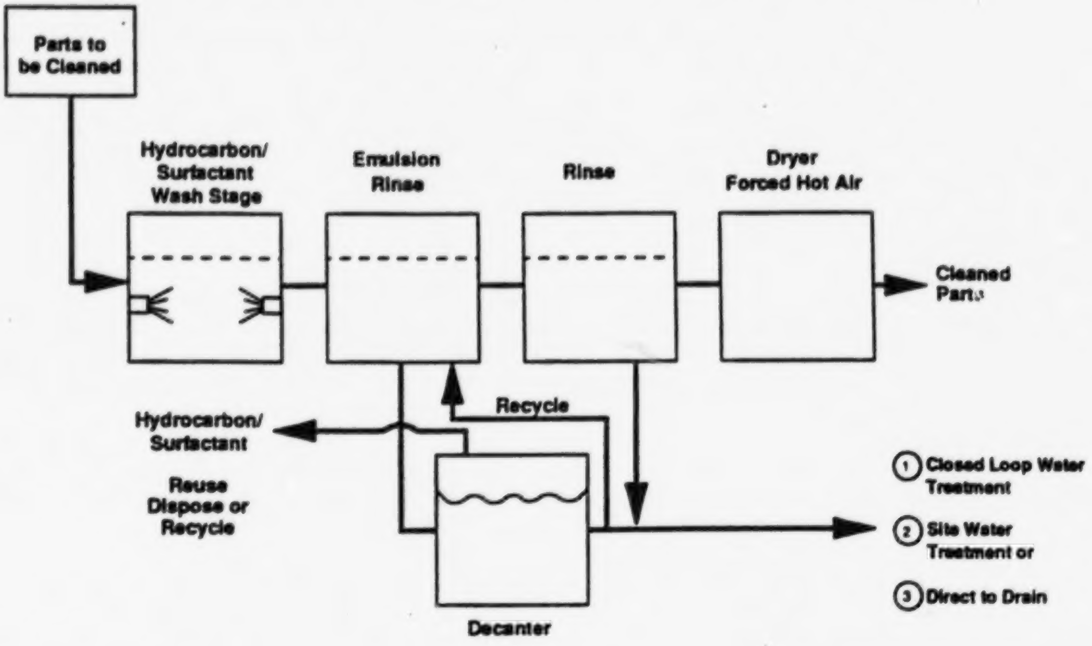
their vapour degreasers for cold cleaning with isopropanol. The refrigeration system of the units remain connected but the heaters are disconnected. This maintains the solvent at more than 20°F below its flashpoint. The equipment is also electrically grounded.

Figure III-4

SEMI-AQUEOUS PROCESS FOR IMMISCIBLE HYDROCARBON SOLVENT


Parts to be Cleaned
Hydrocarbon/ Surfactant Wash Stage
Emulsion Rinse
Rinse
Dryer Forced Hot Air
Cleaned Parts
Recycle
Hydrocarbon/ Surfactant
Reuse Dispose or Recycle
Decanter
① Closed Loop Water Treatment
② Site Water Treatment or
③ Direct to Drain

In the wash step, the hydrocarbon/surfactant cleaner is applied to the part being cleaned with some form of mechanical energy. As a result of the hydrocarbon/surfactant cleaner's high solvency and low flash points, the solvent bath is generally not heated; however, some are slightly warmed when the cleaner is used in a diluted form. Such cleaners are ignitable and should not be used in vapour or spray cleaning without inert atmosphere or other protective equipment. Some semi-aqueous cleaners have flash points above 93°C and can be used hot. Application methods that avoid misting such as spray-under immersion, spin-under immersion, or ultrasonics should be used.

The dilute hydrocarbon emulsion cleaners formulated with water may be heated. Less mechanical energy is needed when using a hydrocarbon/surfactant solution as compared to an aqueous solution because of the high solvency of hydrocarbon/surfactant cleaners.

The clean water rinse step removes the residues left by the wash step. When concentrated hydrocarbon/surfactant cleaners are used, the rinse step is necessary because these cleaners have a low volatility which prevents them from evaporating from the parts cleaned in the wash stage. The rinse step may not be necessary when dilute hydrocarbon/surfactant emulsion is used if the level of cleanliness does not require removal of the residue from the wash stage. In some instances alcohol is used as a final rinse step. The rinse step may also serve as a finishing process and in some instances is used to apply rust inhibitors to the parts.

The drying step serves the same function as it does in aqueous cleaning. Water is removed from the part to prepare it for further processing or to prevent rusting. Heated air and high velocity room temperature air are the principal drying agents. The drying step may not be needed if the parts are rust inhibited and can air dry.

The wastewater disposal step is always an important part of the cleaning process. Most of the contaminants in the wastewater are removed by decanters and filters as the solution is recirculated in the tank.

Because some hydrocarbon/surfactant cleaners can easily be separated by decantation from the rinse water. The rinse water may be recycled or reused, and the waste hydrocarbon/surfactant can be burned as fuel. In such cases, contaminants like oil and grease, removed from the part being cleaned, are retained in the hydrocarbon/surfactant phase, thereby greatly reducing the contaminate loading in the water effluent.

Equipment for use specifically with concentrated hydrocarbon/surfactants is available. As with aqueous cleaning, this equipment can be classified as immersion or spray equipment, and further as batch or in-line equipment. Although there is a temptation to use existing aqueous equipment for the hydrocarbon wash unit, this application is potentially dangerous because of flammability.

Immersion equipment, the simplest design used in hydrocarbon/surfactant cleaning, works with, but is not limited to, dilute emulsion solutions which do not present the combustion (flammability) danger of the concentrated hydrocarbon/surfactants. It can also be used with concentrated hydrocarbon/surfactant cleaners. This equipment may operate in batch or in-line configurations. Some old solvent vapour degreasers can be retrofitted to immerse the parts into the bath of emulsion cleaner. The parts are simply cold dipped into the bath, which may or may not be heated. Because of the solvency of the hydrocarbon/surfactants, very little mechanical energy needs to be added to achieve adequate cleanliness. Higher cleanliness can be achieved by adding agitation to the process, either mechanically with ultrasonics or by heating the wash solution.

As with aqueous cleaning, the mechanical spray action improves the cleaning performance of the solution. When using concentrated hydrocarbon/surfactants, the atomized solution is prone to combustion and special care must be taken to prevent it. Nitrogen blanketing is used to remove oxygen from the spray chamber and the chamber, both of which are enclosed to prevent sparks from entering.

In some instances, "spray-under immersion" can be performed. In this equipment, high pressure spray nozzles are placed below the surface of liquid. This prevents the formation of atomized solution and eliminates flammability.

As in any cleaning application, keep in mind that the best process can be ineffective when used on poorly designed parts. Any process can be improved by a design that reduces the cleaning challenge. This is an important factor, both economically and functionally, and can often be done with low cost during product design.

3.3.4 HCFCs

HCFCs are transitional alternatives since their ozone depletion potential (ODP) values, though small, are not zero. Because of their ODP, HCFCs were recently added to the list of controlled substances under the Montreal Protocol. As a result, they are subject to a phaseout by the year 2030, with a 99.5% reduction by the year 2020. Nevertheless, they have the excellent physical properties of CFCs, such as low surface tension and nonflammability. It is expected, therefore, that some of them can be used in certain applications with minimal or no process changes.

Several HCFCs (e.g., HCFC-225ca/cb, HCFC-141b, and HCFC-123) have been proposed as possible CFC-113 and 1,1,1-trichloroethane substitutes. Table III-3 shows the physical properties of some of these chemicals and compares them with CFC-113 and 1,1,1-trichloroethane. (Note that HCFC-225 is a mixture of two isomers, ca and cb, hereafter referenced as HCFC-225.) A typical composition of HCFC-225 commercially available is a 45/55 percent mixture of the ca/cb isomers. ODP and toxicity of several of these HCFCs will most likely greatly limit or completely eliminate their potential for replacing CFC-113 and 1,1,1-trichloroethane in solvent cleaning applications. Two major manufacturers have limited or cancelled their production of HCFC-123: DuPont will not offer HCFC-123 for cleaning operations, and Allied-Signal has withdrawn all HCFC-123 formulations from the market. In addition, DuPont has said that they will not offer any products containing HCFC-141b.

The advantages of HCFCs in the precision cleaning include the following:

- they exhibit moderate to good cleaning performance
- the CFC-113 cleaning equipment can be used with minor or no modification

Table III-3

PHYSICAL PROPERTIES OF HCFCs AND OTHER OZONE-DEPLETING SOLVENTS

	CFC-113	1,1,1-Trichloroethane	HCFC-225ca	HCFC-225cb	HCFC-141b
Chemical Formula	CCl_2FCClF_2	CH_3CCl_3	$CF_3CF_2CHCl_2$	$CClF_2CF_2CHClF$	CH_3CFCl_2
Ozone-Depleting Potential	0.8	0.1	~0.01	~0.04	0.11
Boiling Point (°C)	47.6	73.9	51.1	56.1	32.0
Viscosity (cps) @ 25°C	0.68	0.79	0.58	0.60	0.43
Surface Tension @ 25°C (dyne/cm)	17.3	25.56	15.5	16.6	18.4
Kauri-Butanol Value	31	124	34	30	76
Flash Point °C	None	None	None	None	None
Toxicity	Very Low	Low	Moderate	Low	Low

- any assembled units with complex shapes and very small clearances can be cleaned well
- the energy consumption of HCFC cleaning systems may be relatively small as compared with those of aqueous and semi-aqueous systems
- they are compatible with most metals and plastics
- HCFC cleaning requires less floor space relative to aqueous and semi-aqueous cleaning
- drying is easy and the assembled units leave no cleaning stains since no water is used during the cleaning process.

The disadvantages of HCFCs include:

- they are a transitional solution; the Montreal Protocol has urged parties to phase-out HCFCs in the period 2020-2040; HCFC-141b has an ODP slightly higher than that of 1,1,1-trichloroethane
- they are volatile and expensive; therefore they usually require retrofitting of the existing equipment or new cleaning equipment; a recovery system will be necessary to minimize the solvent emissions
- they may not be useful in some applications where 1,1,1-trichloroethane is used
- they are incompatible with acrylic resins
- toxicological testing for HCFC-123, HCFC-141b, and HCFC-225 resulted in moderate controls being recommended for these solvents.

HCFC-225 is characterized by the equivalence of CFC-113 in physical properties with ODP values one twentieth that of CFC-113 (Table III-3). It is expected, therefore, that HCFC-225 can be used in most applications where CFC-113 is used without any changes of equipments and processes. Equipment changes would be required, however, to reduce emissions of HCFCs from the equipment. Applications where HCFC-225 might be used include precision cleaning of disk drives, gyroscopes, hydraulic control systems, optical components, electric contacts, plastic assemblies, and applications of special lubricants. Evaluations of HCFC-225 in all these applications are currently in progress.

As mentioned in section 3.2.2.1, recent testing (Schaefer and Scott 1991) has indicated that HCFC-225 is equivalent to CFC-113 in the ability to provide final cleaning before and after vapour deposition coating operations without introducing stains due to solvent evaporation. Successful cleaning of both hard disk drive and hard disk using HCFC-225 has also been reported. Some companies are intending to switch from CFC-113 to HCFC-225 in those applications without a process change. So far, HCFC-225 has received good evaluations as a substitute for CFC-113 in various applications of precision cleaning. There are certain applications in precision cleaning where aqueous and semi-aqueous systems cannot be applied, and HCFC-225 is emerging as a promising substitute in those applications.

It has also been reported that HCFC-225 exhibits poor solvency in some applications. For example, initial testing has shown the HCFC-225 to exhibit poor solubility with the typical blocking waxes and pitches used in the optics manufacturing operation. HCFC-225 is compatible with most metals and plastics but may damage acrylic resins. It cannot, therefore, be applied for cleaning assembled units where acrylic resins are used as the essential material. Compatibility of HCFC-225 with materials which are used in the assembled units to be cleaned should be tested carefully. It has been confirmed that recovery systems for CFC-113 can also be applied for HCFC-225. Also, the recovery system for HCFC-225 has been developed with a 95 percent recovery rate (Yamabe 1991).

The high volatility of some HCFC cleaning solutions require special equipment design criteria. In addition, the economic and environmentally safe use of HCFCs may require special emission control features for vapour degreasers (see Figure III-5). These include:

- Automated work transport facilities
- Hoods and/or automated covers on top entry machines
- Facilities for work handling that minimize solvent entrapment
- Facilities for superheated vapour drying
- Freeboard depth to width ratios of 1.2 to 2.0
- A main condenser operating at 7.2° to 12.8°C
- A secondary condenser operating at -34° to -29°C
- A dehumidification condenser operating at -34° to -29°C (optional)
- Seals and gaskets of chemically compatible materials
- Stainless steel construction
- Welded piping containing a minimum of flanged joints
- A refrigerated desiccant dryer for methanol blends
- A cool room to work in
- Carefully controlled exhaust from the refrigeration unit to prevent excessive heat from reaching the separator chambers.

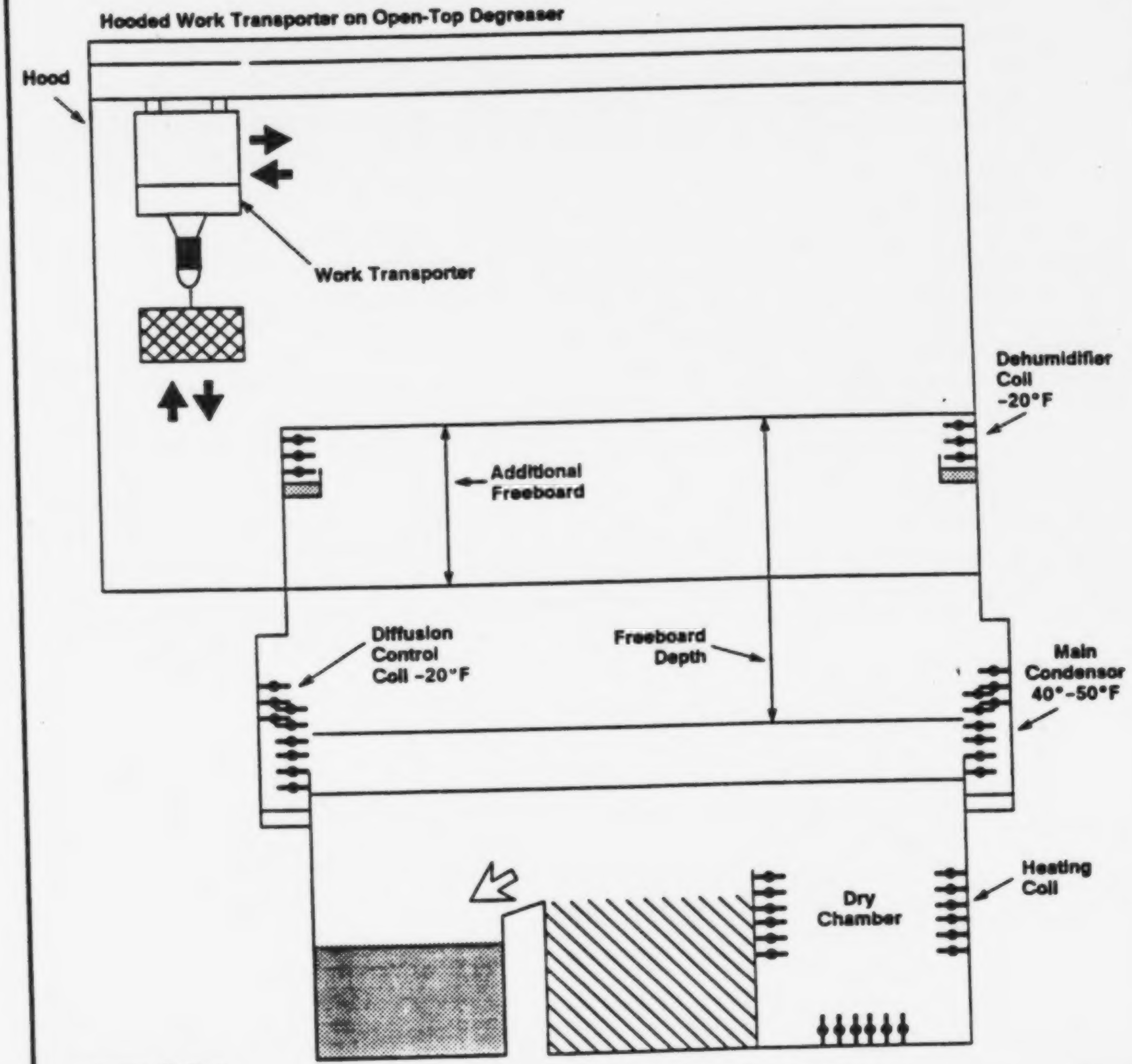
Retrofitting or purchasing a new piece of equipment for use with HCFCs is recommended in many applications. Material compatibility is another important consideration. HCFC-141b requires compatibility testing with magnesium, zinc, and other metals. In addition, the HCFCs have shown some adverse effects with plastics such as ABS, acrylic, and Hi-Impact Styrene. Like metals, plastics need to be tested on an individual basis.

The use of HCFCs in cleaning equipment may be viewed in terms of two distinct equipment categories -- new equipment and retrofitted equipment. Design changes are much easier to implement in new equipment. For example, dual sump open top degreasers (batch units) can have the same working area but different length and width. A degreaser with the lesser width will be more solvent efficient in terms of diffusion losses. It would be impractical, obviously, to consider reorienting sumps on an existing machine in order to take advantage of this design feature. New batch units have the vapour generation sump offset from the rest of the machine, again to help minimize solvent losses. Other features on new equipment are: roll-top lids, gasket-sealed water separator lids, and a P-trap installed in the water drain of the water separator. These features help economize on the use of solvent. A heat exchanger can be used to keep the rinse sump of a batch cleaning unit lower than the boiling point of the solvent by about 10 degrees fahrenheit (24°C).

Some of the features mentioned above (e.g., the roll-top lid, gasket-sealed water separator lid, and P-trap/water drain of the water separator) are readily applicable to retrofitted equipment. In addition, it is relatively easy to extend the working freeboard. Freeboard height is the distance from

Figure III–5

ADVANCED DESIGN DEGREASER FOR USE WITH LOW BOILING POINT SOLVENTS


Hooded Work Transporter on Open-Top Degreaser
Hood
Work Transporter
Dehumidifier Coil -20°F
Additional Freeboard
Diffusion Control Coil -20°F
Freeboard Depth
Main Condensor 40°-50°F
Heating Coil
Dry Chamber

Source: DuPont

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the vapour-air interface line (generally at about the second primary condenser coil) to the lip of the machine. The freeboard ratio is the freeboard height divided by the narrowest dimension of the machine, which is normally the machine width. Freeboard ratio is normally expressed as a percentage.

3.3.5 Alcohols and Ketones

The most common organic solvents are alcohols such as ethanol, isopropanol, and several glycol ethers (methyl, n-butyl, and diethyl). Most of these solvents are chosen for their high polarity and for their very effective solvent power. The alcohols have a range of flash points and care must be exercised while using the lower flash point alcohols (see Table III-4).

Based on material compatibility, alcohols are viable alternatives for component cleaning. Explosion-proof boiling alcohol cleaners using isopropanol could be a practical alternative to CFC-113 and 1,1,1-trichloroethane in many applications. For bulk cleaning of parts at the incoming stage, this alternative could be considered; large-scale isopropanol use may be unacceptable within clean room areas, however, because of flammability risks and operator discomfort resulting from alcohol odours as well as the dehydrating effect of alcohol solvent and vapours on skin surfaces.

Isopropanol and acetone operating in conjunction with ultrasonics have been evaluated as alternatives to CFC-113 in precision cleaning (Mobjork 1989). Care must be taken when using flammable solvents in ultrasonic baths due to the potential for solvent ignition and fires. The following components and instruments were subjected to overall evaluation in this testing:

- Servo component system
- Hydraulic series ram screw
- Accelerometer cut-out
- Horizon indicator
- Horizon gyroscope
- Gyroscope motor components
- Flight position indicator
- Turn and bank indicator
- Reduction vent valve for oxygen
- Oxygen pressure regulator
- Parachute swivel connector.

All components and instruments were retrieved from production except for the oxygen vent and pressure regulator which were manually contaminated. Due to the flammability of isopropanol and acetone, special explosion-proof batch vapour-phase cleaners were used in this evaluation.[8] A number of precision components were cleaned in isopropanol or acetone.

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[8] These ultrasonic vapour-phase cleaners are designed for flammable liquids. The machines are fire- and explosion-proofed according to the DIN-standards and approved by the Federal Republic of Germany's TUV authority.

Table III-4

PROPERTIES OF ALCOHOLS

Product	LB/GAL 15.6°C	SP. GR 20°/20°C	Boiling Range °C	FL. PT. °C TCC	Evap.Rate[1]
Methanol	6.60	0.792	64-65	12	3.5
Ethanol, Prop. Anhydrous	6.65	0.799	74-80	9	1.8
Ethanol, Spec. Industrial Anhydrous	6.65	0.795	75-81	10	1.8
Isopropanol, Anhydrous	6.55	0.786	82-83	12	1.7
n-Propanol	6.71	0.806	96-98	23	1.0
2-Butanol	6.73	0.809	97-102	22	0.9
Isobutanol	6.68	0.803	107-109	29	0.6
n-Butanol	6.75	0.811	116-118	36	0.5
Amyl alcohol (primary)	6.79	0.815	127-139	49	0.3
Methyl Amyl Alcohol	6.72	0.808	130-133	39	0.3
Cyclohexanol	7.89	0.949	160-163	61	0.05
2-Ethylhexanol	6.94	0.834	182-186	73	0.01
Hexanol	7.90	0.950	244-247	120[2]	0.002

[1] N-Butyl Acetate = 1.

[2] C.O.C.

Note: FL. PT. = Flash Pointed Closed Cup Test; SP.GR. = Specific Gravity.

Source: Southwest Chemical Company, Solvent Properties Reference Manual

Cleaned with isopropanol:

- Swivel connector parts contaminated with low temperature grease
- Gyroscope instruments
- Reduction vent valve connections in an oxygen system contaminated with oils and greases
- Oxygen system gas regulators contaminated with soot and char.

Cleaned with acetone:

- Servo-gear piston contaminated with anti-corrosion oil
- Series servo contaminated with hydraulic oils, grease, and particulates
- Accelerometer cut-out contaminated with silicone oil.

Isopropanol proved to be a viable substitute for CFC-113 and generally is compatible with nonmetallics. However, the use of acetone as a viable alternative needs to be studied carefully since it is highly aggressive toward many polymers.

3.3.6 Perfluorocarbons

The perfluorocarbons (PFCs) are a group of fluorine-saturated hydrocarbons (compounds in which all the hydrogen atoms of the hydrocarbon are substituted by fluorine). Because of the extreme electronegativity of the fluorine atom, this saturation results in high chemical stability in all of the compounds. Consequently, they are virtually chemically inert, exhibit low toxicity, are nonflammable, and have zero ozone-depletion potential. As a result of this very low chemical activity, PFCs can be used in medical applications and are safe in contact with pure oxygen at high pressures. Their stability, however, makes PFCs extremely potent global warming compounds. Due to their high global warming potential (GWP), the use of PFCs is being restricted in a number of countries.

Choice of base hydrocarbon provides a wide range of molecular weight and molecular structure resulting in a range of boiling points. Table III-5 shows some of the basic properties of PFCs that were commercially available in late 1994.

Besides their GWP, another major disadvantage of PFCs is their high cost which is a result of the complex synthetic production processes. A typical low- to mid-range boiling PFC, for example, is approximately \$26 to \$40 US per kg (late 1994). The high cost of these compounds should encourage potential users to use PFCs only in vapour-tight equipment, reducing the amount of PFCs that are lost to the atmosphere. Another drawback is that PFCs have very low solvency power for hydrocarbons and are unlikely to be very useful for removing oils. They have been shown, however, to be excellent solvents for perfluoropolyethers and other halogenated compounds.

Where no other substitutes are feasible, PFCs offer possible solutions to current CFC-113 and 1,1,1-trichloroethane users, particularly in cleaning parts for high accuracy gyros. Some current high density flotation fluids are soluble in certain PFCs, which can therefore be used for flushing filled

Table III-5

Properties of Perfluorocarbon Solvents Available in 1994

Basic Formula	$C_5F_{11}NO$	C_6F_{14}	C_7F_{16}	C_8F_{18}	CFC-113	1,1,1-Trichloro-ethane
Ozone Depletion Potential	0	0	0	0	0.8	0.10
Global Warming Potential[1]	6000	5200	4900[2]	4700[2]	4500	100
Boiling Point, °C	50	56	80	101	47.6	73.9
Density, g/ml, 25°C	1.70	1.68	1.73	1.77	1.57	1.33
Viscosity, cP, 25°C	0.68	0.67	0.95	1.4	0.68	0.79
Surface Tension, dynes/cm, 25°C	13.0	12.0	13.0	15	19.0	25.6
Silicone Solubility	Very Low	Very Low	Very Low	Very Low	High	Moderate
Fluorocarbon Solubility	High	High	High	High	High	High
Solubility Parameter, H	6.3	5.6	5.7	5.7	7.3	7.7
Flash Point, °C	None	None	None	None	None	None
Approximate Cost, US$/kg	23	23	23	23	22	7

[1] Based on 100-year time horizon.
[2] Estimated

Source: 3M

assemblies. In addition, high pressure spraying with PFCs appears to be a very effective method of particle removal. The excellent chemical stability of these fluids makes them compatible with all gyro construction materials including beryllium. Table III-6 summarizes the compatibility of PFCs with various materials.

Design of equipment for gyroscope or other precision parts cleaning will have to be specific to each application. Whatever type of equipment is designed, it should be a vapour-tight system to facilitate reclamation and recycling. The chemical stability of PFCs makes them excellent compounds for recycling. Currently, suppliers offer reclamation and recycling programs for these compounds, thus minimizing emissions that could contribute to global warming.[9] If vapour-tight equipment is not utilized, the evaporative loss of PFC would be prohibitively expensive and would make the use of PFCs very difficult to rationalize (even considering the high cost and strategic importance of the products).

3.3.7 Isopropyl Alcohol Cleaning with Perfluorocarbon

Alcohols such as ethyl and isopropyl have been used extensively for cleaning printed circuit boards and precision components. They are very effective in removing rosin and polar activators commonly used in flux. Safety is the primary difficulty in using alcohols because of their high flammability. In order for alcohols to become viable options, both flame and explosion proofing are necessary expenditures to prevent operator injury and equipment damage. Using a perfluorocarbon (PFC) "blanket" in suitable equipment renders the alcohol vapour nonflammable, and results in a safer alcohol vapour degreaser.

The advantages of using this type of process include:

- Isopropyl alcohol, being extremely polar, has good solvency and allows for the removal of differing types of particulate and organic contamination than CFC-113.
- PFCs are nonflammable, have low toxicity and reactivity, and have zero ozone-depleting potential.
- The nonflammable nature of the alcohol-PFC vapour allows a safe, continuous distillation at a lower temperature than isopropyl alcohol alone with rapid rinsing to give a dry product.
- PFC and isopropyl alcohol are virtually non-immiscible; PFC being more dense forms a layer below the alcohol. If this lower PFC layer is heated to its boiling point (approximately 50°C), the vapour generated will entrain the alcohol to form a mixed vapour with approximately five percent alcohol at a temperature of 50°C. This layer is nonflammable.

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[9] Preliminary studies by one equipment manufacturer have demonstrated emission reductions of 90 percent for PFCs compared to historical emissions of CFC-113.

Table III-6

PERFLUOROCARBON (PFC) COMPATIBILITY WITH VARIOUS MATERIALS

Class of Material	Observation
Rubbers	<1 percent linear swell, ± 1 percent change in weight
Polyethylene, polypropylene	<1 percent shrinkage, zero change in weight
Nylons	Negligible change in dimensions or weight
Polystyrene	Variable, generally negligible, shrinkage (e.g., 0.2 percent)
"Perspex" ("Plexiglass")	<0.2 percent shrinkage, slight loss in weight
FTFE (unfilled)	2-3 percent linear swell, up to 10 percent increase in weight
PVC (Rigid)	Negligible change
PVC (Flexible)	Extraction of plasticizer, loss of flexibility (in hot Flutec)
Electronic circuit boards*	± <0.1 percent dimensional change, zero change in weight
Copper and brass	Slight tarnishing (from dissolved oxygen)
Other Common metals	No effect detectable
Silicone and microcircuit chips	No known effect
Adhesives Adhesive tapes Paper Enamelled wires Insulating tapes Paints Other surface coatings and sealants	No adverse effects detected in any samples tested up to the present time

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* Including: SRBP, Epoxy, DAP, Silicone, Melamine, Polyester, with filler materials of all common types.

Source: Rhone Poulenc, ISC Chemicals Division

- Alcohol and PFC are "clean" agents; i.e., they leave no residue. They also evaporate readily at low temperatures.

- Additional features of some equipment include a hermetically sealed lid, under lid basket operation, and a balancing volume to accommodate volume changes on heat-up and shut-down. Superheated PFC spray can also be used to facilitate removal of isopropyl alcohol from cleaned parts.

The disadvantages include:

- A properly designed, dedicated piece of equipment consisting of a conventional two-tank vapour degreaser with a boiling alcohol (soiled solvent) tank and a pure hot alcohol rinse tank is required to operate this process.

- Safety systems must be designed to automatically cease operations should the PFC level drop below the level necessary to prevent explosion.

- Pure alcohols are not effective at removing nonpolar contaminants like grease and flux residue. However, cleaning effectiveness can be enhanced by combining the alcohol/PFC cleaner with a precleaner unit using hydrocarbons or other solvents.

- PFCs have a high global warming potential and atmospheric lifetime.

- PFCs are expensive, currently priced from US$26.00/kg.

3.3.8 Aliphatic Hydrocarbons

Aliphatic hydrocarbons, which offer tighter control on composition, odour, boiling range, evaporation rate, etc., are employed in original equipment manufacturer (OEM) cleaning processes and will be discussed below. The advantages of aliphatic hydrocarbon cleaners include:

- Compatible (non-corrosive) with most rubbers, plastics and metals
- Employs no water, hence can clean water-sensitive parts
- Low odour and low toxicity grades available
- Reduced evaporative loss
- No wastewater stream
- High stability and recovery
- Recyclable by distillation
- Good cleaning ability for wide variety of soils, especially heavy grease, tar, waxes, and hard to remove soils. Low surface tension allows good penetration.

The disadvantages include:

- Flammability concerns (can be solved with proper equipment design)
- Slower drying times than halogenated solvents
- VOC control may be required. However, equipment such as carbon adsorption and condensers can recover solvent from effluent air

- Low occupational exposure limits are associated with some grades.
- Waste products are classified as hazardous waste

A wide range of aliphatic hydrocarbon solvents are used in precision cleaning (see Table III-7). Petroleum fractions, commonly known as mineral spirits or naptha, are used extensively in maintenance cleaning. These are single stage, open top processes using ambient air drying. In most cases such processes are not suitable for Original Equipment Manufacture (OEM) cleaning.

The major steps in the hydrocarbon cleaning process are washing (1-3 stages depending on degree of cleaning needed) with a hydrocarbon cleaner, drying using forced air, VOC recovery from solvent-laden air, and waste-solvent recovery or disposal. The wash steps involve liquid-phase cleaning at temperatures sufficiently below the flash point of the fluid. Ultrasonics or other agitation processes such as immersion spraying, parts rotation, or fluid pump around can be used to augment cleaning action. (However, note that ultrasonic equipment manufacturers do not recommended the use of ultrasonics with flammable solvents.) Spraying or misting processes, where fine droplets are formed, should be employed only in an inert environment or with equipment otherwise protected from ignition conditions, because fine droplets can be ignited at temperatures below bulk fluid flash point.

Fluids with flash points near 40°C (104°F) or below should be used in unheated equipment operating at ambient temperatures, although the continued use of refrigeration coils is preferred. For higher flash points, hot cleaning can be employed to boost cleaning action. For systems with good temperature control (independent temperature sensors, cutouts, level indicators, etc.), a safety margin of 15°C (59°F) between the fluid flashpoint and the cleaning temperature, or 90 percent below the lower explosive limit (LEL), is recommended. For systems with poorer temperature control, a higher margin should be employed.

Each wash step should be followed by a drain period, preferably with parts rotation, to minimize solvent dragout from stage to stage.

In multistage processes, fluid from one bath is periodically transferred to the preceding bath as its soil level builds up. Fresh solvent is thus added only to the final bath to ensure the highest parts cleanliness, and spent solvent is only removed from the first stage.

The drying step normally uses forced air which may be heated. Either the dryer should operate at 15°C below the flash point of the fluid, or sufficient air flow should be provided so that the effluent air composition is well below the Lower Explosive Limit (LEL) of the system.

The VOC recovery step is an important part of the cleaning process. Depending on the solvent chosen, either carbon adsorption or condensation are the best technologies for recovery of solvent vapours from spent drying air and lip vent air. There are numerous vendors of such recovery equipment.

In the waste recovery area, the best reclamation technology for these products is usually filtration and distillation. One of the advantages of the low olefin content and narrow distillation range is that the recovery in distillation is high. Should some disposal of residual solvent be necessary, fuel substitution or incineration are good routes.

Table III-7

PROPERTIES OF ALIPHATIC SOLVENTS

Product	LB/GAL 15.6°C	SP. GR 15.6/15.6 °C	Boiling Range °C	FL. PT. °C TCC	KB	Evap. Rate[1]
Mineral Spirits	6.37	0.764	152-202	41	32	0.1
Odourless Mineral Spirits	6.33	0.760	177-202	53	27	0.1
140 Solvent	6.54	0.786	182-210	60	30	0.1
Kerosene	6.60	0.790	166-257	54	30	0.19
C10/C11 Isoparaffin	6.25	0.750	160-171	42	29	0.3
C13 N-Paraffin	6.35	0.760	227-238	93	22	0.1
C10 Cycloparaffin	6.75	0.810	166-182	41	54	0.2

[1] N-Butyl Acetate = 1.

Note: FL. PT. = Flash Point Closed Cup Test; KB = Kauri-Butanol Value; SP.GR = Specific Gravity.

Sources: Southwest Chemical Company, Solvent Properties Reference Manual; Exxon Chemical Company

3.3.9 Chlorinated and Other Miscellaneous Organic Solvents

The precision cleaning industry has always used a very wide range of miscellaneous solvents. In all applications such solvents are used for manual operations, usually by means of camel or sable hair brushes during assembly or rework. In addition to those already described, other chlorinated solvents, ethers, ketones, alcohols, and esters, are also candidate replacements for precision applications. Typical uses are local defluxing after solder rework operations, defluxing after special solder operations (e.g., strain gauge lead attachment), and varnish applications (e.g., small scale in-situ coil impregnations).

The chlorinated solvents that do not destroy the ozone layer – trichloroethylene, perchloroethylene, and methylene chloride (dichloromethane) – also are effective cleaners. Because of their widespread use, they have been scrutinized for their safety, health, and environmental impacts. Many countries have established exposure levels that are considered safe for workers. In addition, many countries have placed additional controls on emissions to the atmosphere from processes using these solvents. Local regulations, Material Safety Data Sheets, and industrial recommendations such as those of the American Conference of Governmental Industrial Hygienists should be used as guidance in establishing safe handling and usage procedures for these solvents.

The development of extremely low emissions cleaning equipment which minimizes worker exposure levels, and emissions to the environment, along with good management practices offers users an alternative that provides for equivalent or better cleaning with existing technology. The combination of limits being placed on users will require their use only in applications where emissions are very carefully controlled. Table III-8 summarizes the properties of these other chlorinated solvents.

The ketones (see Table III-9) form a group of very powerful solvents. In particular, acetone (dimethyl ketone) and methyl ethyl ketone are very good solvents for polymers and adhesives. In addition, acetone is an efficient dewatering agent. However, their extreme flammability (note that acetone has a flash point of -18°C) and incompatibility with many structural polymers (e.g., stress-cracking of polyether sulphone, polyether ketone, and polycarbonate) means that they should only be used with care and in small quantities. Consequently, large-scale use as CFC-113 or 1,1,1-trichloroethane alternatives would be unlikely.

Esters such as dibasic esters have good solvent properties. Most of these materials are readily soluble in alcohols, ketones, ethers, and most hydrocarbons, but are only slightly soluble in water and high paraffinic hydrocarbons. The materials have high flash points and low vapour pressures. Dibasic esters, however, are so low in vapour pressure that a residual film will remain on a surface after application. In addition, they have been found to be genotoxic and should therefore be used with caution.

3.3.10 Pressurized Gases

Particulate contamination may be removed with pressurized gases as an alternative to cleaning with CFC-113 and 1,1,1-trichloroethane. However, the use of these gases will not generally remove ionic or organic contamination

Table III-8

PROPERTIES OF HALOGENATED CHLORINATED SOLVENTS

Physical Properties	CFC-113	1,1,1-Trichloroethane	Trichloroethylene	Perchloroethylene	Methylene Chloride
Ozone-Depleting Potential	0.8	0.1	0	0	~0
Chemical Formula	CCl_2FCClF_2	CH_3CCl_3	$CHClCCl_2$	CCl_2CCl_2	CH_2Cl_2
Molecular Weight	187.38	133.5	131.4	165.9	84.9
Boiling Point (°C)	47.6	72-88	86-88	120-122	39.4-40.4
Density (g/cm^3)	1.56	1.34	1.46	1.62	1.33
Solubility Parameter, Hildebrands	7.7	9.2	9.3	9.7	9.7
Surface Tension (dyne/cm)	17.3	25.4	29.3	31.3	N/A
Kauri Butanol Value	31	124	130	91	132
Toxicity	Low	Low	Medium	Medium	Medium
Carcinogenicity	No	No	See Note[a]	See Note[b]	See Note[c]
Flash Point (°C)	None	None	None	None	None

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[a] The U.S. EPA has not formally classified trichloroethylene in Category B2 as a "probable human carcinogen," while the International Agency for Research on Cancer (IARC) has classified this solvent in Group 3, a substance not classifiable as to its carcinogenicity in humans.

[b] The U.S. EPA has not formally classified perchloroethylene in Category B2 as a "probable human carcinogen." IARC has classified perchloroethylene in Group 2B as a substance considered "possibly carcinogenic to humans."

[c] The U.S. EPA has classified methylene chloride in Category B2 as a "probable human carcinogen," while IARC has classified methylene chloride in Group 2B as a substance considered "possibly carcinogenic to humans."

Source: UNEP (1989).

Table III-9

PROPERTIES OF KETONES

KETONE	Formula	Mol. Wt.	lbs per gal	B.P. °C	Flash Point °C open cup	Evap Rate $CCl_4=100$	Solubility Parameter H	Surface Tension 20°C Dynes/cm
Acetone	C_2H_6CO	58.08	6.58	56-57	-17	139	9.9	23.7
Methyl Ethyl Ketone (MEK)	C_3H_8CO	72.10	6.71	79-81	-2.2	97	9.3	24.6
Diethyl Ketone	$C_4H_{10}CO$	86.13	6.80	100-104	12.6	-	8.8	24.8
Methyl n-Propyl Ketone	$C_4H_{10}CO$	86.13	6.72	101-107	7.2	66	8.7	25.2
Cyclohexanone	$C_5H_{10}CO$	98.14	7.88	130-172	62	12	9.9	-
Methyl Isobutyl Ketone (MIBK)	$C_5H_{12}CO$	100.16	6.68	112-118	17.6	47	8.4	22.7
Methyl n-Butyl Ketone	$C_7H_{12}CO$	100.16	6.83	114-137	22.5	32	8.3	25.5
Methyl Cyclohexanone	$C_6H_{12}C0$	112.17	7.67	114-173	47.3	7	9.3	-
Acetonyl Acetone	$C_4H_{10}(CO)_2$	114.14	8.10	185-195	78	-	-	39.6
Diisopropyl Ketone	$C_6H_{14}CO$	114.18	6.73	114-127	23.6	-	8.0	-
Methyl n-Amyl Ketone	$C_6H_{14}CO$	114.18	6.81	147-154	48.4	15	8.5	-
Diacetone	$C_5H_{12}CO$	116.16	7.82	130-180	8.8	4	-	29.8

Source: DuPont, A.F. Barton, Handbook of Solubility Parameters and Other Cohesion Parameters, CRC Press (see the section on supercritical fluids). Primary considerations for choosing pressurized gases depend on the following properties:

- **Surface chemistry**. This factor is ultimately responsible for the nature of the electrostatic forces between surfaces.

- **Porosity**. Porous (and rough) surfaces possess the potential to mechanically lock contaminant and substrate and further hinder the cleaning process.

- **Roughness of surface**. Large particles on a smooth surface may be removed more easily than small particles on a rough surface for the same reason.

- **Size, shape, and homogeneity of the contaminant**. On a microscopic level, all surfaces possess ridges and valleys that make intimate contact between surfaces difficult. Adsorbed contamination on particles and other surfaces also hinders contact and prevents relatively short-range molecular interactions from occurring.

- **Sensitivity of the surrounding area to ejected material**. Relatively inert gases and mixtures are most often used with specially designed equipment to meet the cleanliness requirements of the surrounding area.

Depending upon which pressurized gas is used in the cleaning application, the advantages of using pressurized gases versus halogenated solvent cleaning could include the following:

- Low viscosity
- Low toxicity
- High diffusivity
- Nonflammability
- Low capital cost.

The disadvantages of using pressurized gases could include:

- Low density
- High pressure (rupturing of seal)
- Cleaning of critical components
- Often not effective for microscopic particles
- Safety considerations.

Possible Gases:

Gases which may be used include air, rare gases, carbon dioxide, chlorodifluoromethane (HCFC-22), and nitrogen. These gases are readily available in bulk and smaller quantities and in numerous grades of purity. These gases may be stored at room temperature. Dry air is produced from ordinary air by removing hydrocarbons by oxidation. Carbon dioxide is then removed and the air is compressed and dried.

Because of its oxygen content, air reacts with many substances, rare earth gases, however, are noted for their extreme chemical inactivity. These monatomic gases are helium, neon, argon, krypton, and xenon and may be obtained by fractionation of liquid air. Argon, the most abundant of the rare earth gases, is commercially available in cylinders ranging from 1,775 to 6,000 psig at 21.1°C. Argon is not toxic, but is an asphyxiant and is heavier than air.

Carbon dioxide, which is recovered from a number of processes, is colourless, odourless, nonflammable, and slightly acidic. The gas is stable under most conditions, but it will dissociate into carbon dioxide and carbon monoxide in the presence of free carbon at high temperatures. For example, at 100°C, the equilibrium ratio of carbon dioxide to carbon monoxide is 0.7 percent to 99.3 percent. Above the critical temperature of 31°C, all solid carbon dioxide converts to a gas. It may be shipped under its own vapour pressure of 830 psig at 21.1°C. Caution must be taken in dealing with carbon dioxide since it acts as an asphyxiant and cumulative amounts of the gas can act like a poison. Note that the use of carbon dioxide does not contribute to global warming because the source of the most carbon dioxide is the air itself.

Colourless and nonflammable, HCFC-22 has an ozone-depletion potential of 0.05. At high temperatures, various metals may catalyze decomposition of the gas. Silver, brass, bronze, aluminum, 1340 steel, copper, nickel, 18-8 stainless steel, and inconel react in descending order, with silver being the most reactive. Magnesium and aluminum alloys with two percent or more magnesium are particularly reactive in the presence of water. Natural rubber may also be swollen and degraded by the solvent. Continued flooding of localized areas with liquid produces rapid chilling. This feature may be desirable to remove more tenacious contaminants. It is often shipped as a liquified gas under its own pressure of 123 psig at 21.1°C. The gas is available in bulk and small disposable cans. Direct contact with liquid chlorodifluoromethane may cause frostbite. The gas is considered to be nontoxic, but high concentrations can produce dizziness, narcosis, and nausea.

Equipment Considerations:

Clean dry air may be economically produced from pressurized air in-house. Specifically designed diaphragm and other noncontaminating pumps are available. High efficiency filters, drying agents, and other equipment can be used for most of these gases.

A problem inherent in cleaning with high pressure gases is the development of static charges. Ionizing guns that can alleviate this problem are available from clean room equipment suppliers.

Typically, clean, dry, inert gas, or air is fed to a pressurized gas gun at 689.5 kPa. Many models offer 0.3 to 0.5 micron particle filtration with a maximum outlet pressure of ionized gas at 207 kPa. Different ionizing and filtration techniques have been designed for specific needs. One model is reported to remove 3.0 micron size particles with 99 percent efficiency from bare silicon wafers.

Composition of the contaminant and substrate may determine whether or not ejected material produced by pressurized gas will damage surrounding surfaces. Metal dust may be easily removed from an assembly with pressurized gas. However, if an optical component with a sensitive coating is part of the assembly, it could be scratched by impinging particles. Particles with low mass may not present a problem. Likewise, harder components may be resistant enough to allow this process. Consideration of dislodged particles is not limited to resistance of the assembly or part because clean room requirements, as well as surrounding structure, may not tolerate increased levels of contamination.

Containment of ejected debris may be accomplished for small parts by operating the process in a laminar flow work station equipped with a high efficiency particulate air filter or an ultra-low penetration air filter. Vacuum may also be used with pressurized gas on some parts to capture dislodged contamination.

3.3.11 Supercritical Fluids

The use of supercritical fluids (SCF), especially carbon dioxide, has escalated in the early 1990's. SCFs are chemicals that are normally liquid or gaseous at standard temperature and pressure. However, when the pressure and temperature are increased to specific levels, the chemical reaches a supercritical state and exhibits very different solvent properties. Table III-10 lists some of the data for typical supercritical solvents.

In the case of supercritical carbon dioxide (CO_2), the fluid has been used for many years in the food and flavour industry. One example is the use of supercritical CO_2 to decaffeinate coffee. The properties of the SCFs are such that at each temperature and pressure combination within the supercritical region, the fluid behaves with slightly different solvency powers. In the coffee decaffeination example cited above, the coffee beans are loaded into a very large, high pressure reactor. The CO_2 is injected into the reactor and the pressure and temperature are simultaneously increased. The coffee bean flavour – an organic chemical itself – is first removed from the beans by adjusting the pressure and temperature and then releasing the carbon dioxide to a capture chamber, where the flavour is held. Then, the reactor is refilled with CO_2, and adjusted to a different temperature and pressure and the caffeine is removed and captured into another holding chamber. Finally, the pressure and temperature combination of the coffee flavour is readjusted and the flavour is added back to the beans.

The equipment for a supercritical CO_2 cleaning system can start at between $60,000 to $120,000 for small reactors of approximately 1 cubic foot capacity. The cost of the unit depends on the types of soil to be removed and the size of the high-pressure reactor. It is common for the reactors to be operated in the 2000 to 5000 psi range with temperatures between 40°C to 110°C.

Compared to liquid solvents such as CFC-113 and 1,1,1-trichloroethane, SCFs have a higher diffusivity and a much lower density and viscosity. This combination of characteristics allows for rapid extraction of contaminants and phase separation. Other chemicals, such as nitrous oxide, ethane, ethylene, and water, can be used in supercritical cleaning processes, but CO_2 has proven to be the safest, the most abundant and economical, and very effective. Supercritical fluids display the following properties:

- wide range of solvent solubilities
- gas-like diffusivity
- zero surface tension

Table III-10

DATA FOR TYPICAL SUPERCRITICAL SOLVENTS

Solvent	Critical Temperature (deg. C)	Critical Pressure (atm)	Density (g/cm3)
Methane	-83	45.4	0.16
Ethylene	9	49.7	0.22
Chlorotrifluoromethane	29	38.7	0.58
Carbon dioxide	31	72.8	0.47
Ethane	32	48.2	0.20
Nitrous oxide	36	71.5	0.45
Sulfur hexafluoride	45	37.1	0.74
Propylene	92	45.6	0.23
Propane	97	41.9	0.22
Ammonia	132	111.3	0.24
Trichlorofluoromethane	198	43.5	0.55
n-Hexane	234	29.3	0.23
Isopropanol	235	47.0	0.27
Ethanol	243	63.0	0.28
Toluene	318	40.6	0.29
Water	374	217.7	0.32

- short process times
- low energy costs
- does not generate waste products (except for the contamination removed)
- gas is completely recoverable

SCFs exhibit many properties of an ideal process, however the high cost of the equipment and the necessary process development to fine-tune the cleaning process will require significant funding. Some characteristics of the SCF process that should be considered include potential material compatibility problems and the necessary training for operators of the high-pressure equipment. SCF processes should be targeted to industries where expensive fluids are to be removed from precision hardware, specifically the medical, space, and defense industries.

Test results obtained by one company using SCF cleaning for developmental tests on precision gyroscopes for high-reliability use indicate the following:

- effective removal of oils and polyhalogenated fluids
- pressures and temperatures required
  -- perfluoropolyether oils ... 1500 psi, 170 °F
  -- halogenated and other oils ... 3500 psi, 185 °F
- incompatible with hermetically sealed devices
- epoxy weight gains detected of greater than 2.5 percent
- effective for deep pores (width/diameter of 650 to 10,000)
- material compatibilities
  -- metals, ceramics, and glass were good
  -- thermoset plastics were good
  -- thermoplastics were fair to good
  -- elastomers (rubber) were bad, except for silicones

Supercritical carbon dioxide has been tested by several users as a potential replacement for precision cleaning with CFC-113 and 1,1,1-trichloroethane. Table III-11 illustrates the types of applications that have been successful. It is important to confirm that the cleanliness achieved in each application matches the precision cleaning requirements.

Process Overview:

Figure III-6 shows a generic supercritical carbon dioxide cleaning process. Carbon dioxide is pressurized and heated to its supercritical state and introduced into the extraction vessel at the selected extractor operating conditions. In the extractor, the supercritical fluid selectively extracts one or more components from the source material. The solute-rich gas exits the extractor and undergoes a temperature and/or pressure change. This change decreases the solubility of the solute in the fluid and, due to the change in solubility, a solute/fluid separation takes place in the separator vessel.

In order to determine whether SCF is a technically feasible and economically viable alternative, it is necessary to evaluate phase equilibrium properties of the fluids. These include the number of phases present, the composition and density of each phase, and the equilibrium changes associated with temperature, pressure, and composition. This is important because of the often complex behaviour of fluids in high-pressure phase. Phase equilibrium

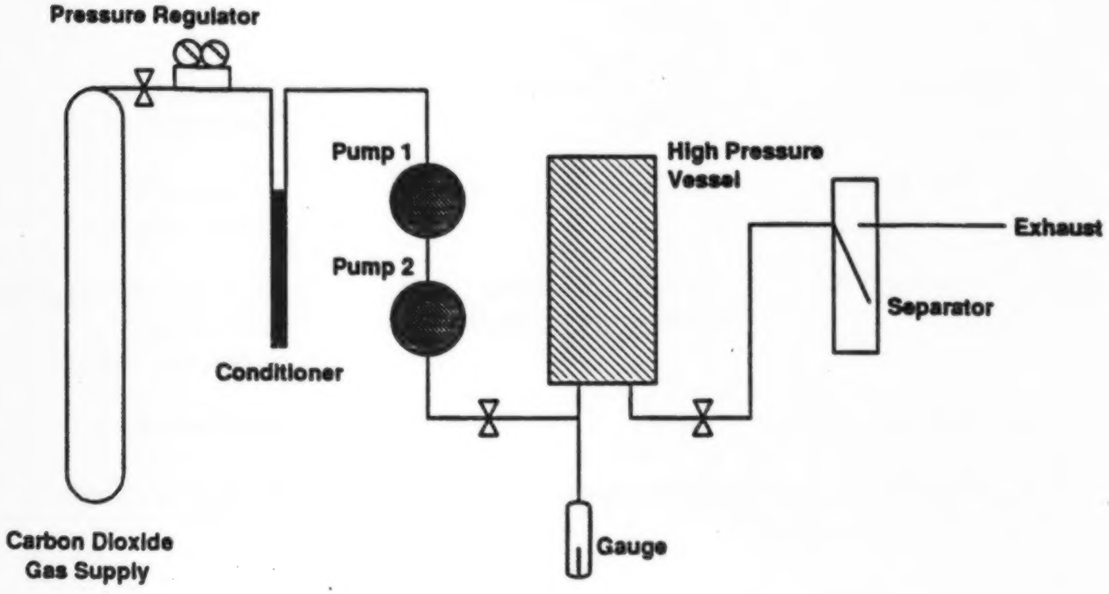
Table III-11

SUPERCRITICAL CARBON DIOXIDE APPLICATIONS

Hardware	Materials/Components Cleaned	Contaminants Removed
Spacecraft	High voltage cables Bearings Rivets	Silicone oils Lubricants
Radar	Connectors Transformers Cables	Flux residues Dielectric oils
Laser	Optical benches O-rings	Machine oils Plasticizers
Gas system	Seals	Plasticizers Monomers
Cleaning aid	Cotton ball/wipers Cotton tipped applicators	Organic extractables Triglycerides Adhesive residues
Nuclear	Valves	Radioactive Oil
Missiles	Gyroscopes	Perfluoropolyethers

Figure III-6

BASIC MODEL DESIGN FOR CARBON DIOXIDE SUPERCRITICAL CLEANING SYSTEM


Pressure Regulator
Pump 1
High Pressure Vessel
Exhaust
Pump 2
Separator
Conditioner
Carbon Dioxide Gas Supply
Gauge

Source: Jackson 1987

116005-21

and mass transport data is used to size equipment, determine utility requirements, and estimate costs.

The pressure-dependent dissolving power of CO_2 is not limited to polymers and oils of only medium molecular weight and materials of low polarity. Very highly polar materials such as alcohols and organic acids are soluble, and among polymeric materials, many polymers and high molecular weight oils, such as silicones and fluoroethers, commonly associated with gyroscopes are soluble; silicones of several hundred thousand MW dissolve to high levels in supercritical CO_2. For completeness here, SC CO_2 can dissolve many hydrocarbons, esters, silicones, perfluorinated oils, halocarbon-substituted triazines, and polychloro- and bromo-trifluoroethylene; these materials can also be fractionated based on molecular weight which has special purpose application in lubrication and coating. While there are polymers that are insoluble in CO_2, some of them – depending on the degree of cross-linking and crystallinity – may exhibit swelling and/or incompatibility in CO_2.

Unfortunately, there are also many confusing claims which continue to be perpetuated throughout the literature and patents regarding the ability of SC CO_2 to dissolve particulates (e.g., lint, dust, scale, metal, and salts, etc.), fluxes, and other materials. While it is possible that some dislodging of particulates can occur due to velocity forces, they do not dissolve in CO_2. Based on extensive investigation with rosin based fluxes, it can be stated with certainty that these materials are insoluble in carbon dioxide. Some of the confusion may arise because of incompletely understood phenomena. For example, abietic acid (the main component of rosin) is soluble in CO_2 and it is interesting that a recent international patent application has stated that abietic acid must be modified with methanol to impart any reasonable solubility in CO_2. The confusion arises because after exposure to high temperatures required for reflowing solder flux, abietic acid can polymerize enough to render the flux residue insoluble. Even many low solids and water soluble fluxes are insoluble in CO_2; thus SC CO_2 is not generally applicable to circuit board cleaning (although in special cases it may show limited results.)

3.3.12 Plasma Cleaning

A plasma is an electrically charged gas containing ionized atoms, electrons, highly reactive free radicals, and electrically neutral species. Plasma, produced by passing an electric current through a process gas, is characterized by high reactivity and a specific frequency of electromagnetic radiation, usually in the UV and visual light bands. Common examples of plasma are fluorescent lighting, neon signs, and the solar corona.

Plasmas can exist in a wide variety of pressure and temperature conditions, but "cold" plasmas are best for cleaning applications. These typically have temperatures under 60°C. Normal operating pressures are 1-5 mmHg, under an atmospheric pressure of 760 mmHg. Such operating conditions are easily produced.

The cleaning process consists of six steps:

- Evacuating the chamber to base vacuum pressure
- Introducing process gases and then stabilizing them at operational pressure
- Irradiating the chamber with radio frequency energy to produce the plasma -- a step that causes the process gas to flow through the chamber removing compounds such as carbon monoxide, carbon dioxide, and water vapour
- Shutting off radio frequency energy and process gases and returning to base pressure
- Purging the chamber with a nonreactive gas such as nitrogen to remove all traces of volatile compounds
- Returning to atmospheric pressure and then venting to atmosphere.

The third step is the actual cleaning portion of the procedure. The ions and electrons in the plasma are energized by the radio frequency radiation to energy levels of approximately 1 eV. The bonds found in organic contaminants, C-C, C-H, and C-O, have energies from 3 to 5 eV. The high reactivity of the ions, combined with their kinetic energies, is sufficient to break these organic bonds. The ions then react with the freed atomic components and form volatile compounds which are then removed by the flow of the process gas.

The advantages of plasma cleaning include:

- Process gases are relatively cheap, nontoxic, and noncaustic. Example gases are oxygen, argon, helium, silicon tetrafluoride, and air.
- Only small amounts of process gas are required for each cleaning. This amount will vary with exposure time and size of enclosure.
- Low operating costs compared to solvent cleaning. No disposal procedures are necessary.
- The cleaning time depends greatly on the specific process, but generally ranges from a few seconds to a few hours.
- Because the plasma is essentially gas-like, all shaped parts are cleaned simultaneously and evenly. Because the cleaning takes place on the molecular level, all features, regardless of size, are cleaned equally well.

The disadvantages of plasma cleaning include:

- Capital costs are initially high and the equipment is highly specialized. Reactor costs are typically $20,000 to $130,000.

- For space systems such as satellite optical components that must be cleaned during use, the plasma gases must be provided at launch or produced chemically.

- Contaminant layers are not cleaned at an even rate. It may be difficult to determine exactly how long the process should last. Outer layers are stripped faster, and at lower energies, than layers close to the original surface. A possible reason for this could be that the inner layers are exposed to more UV radiation from the plasma itself, and therefore cross-polymerize and form stronger bonds with the surface. For space systems, this uncertainty could lead to overuse of limited process gas supplies.

- Plasma is not formed efficiently in hidden areas of complex parts and diffusion of plasma into these areas is slow.

- Using oxygen as a process gas produces a visible film on the surface of gold mirrors. Such a film may be difficult to remove and, if left on the mirror, may increase light scattering.

- The energy of the process must be limited to avoid sputtering, a phenomenon that can damage the elements being cleaned.

- Because cleaning capacity is low, gross contamination should be removed prior to plasma cleaning.

- Operator training will be required.

A plasma cleaning system usually consists of a reactor, a radio-frequency generator, and a control system. The reactor, which can be cylindrical or planar, must hold the components for cleaning. The radio-frequency generator supplies the energy for creating plasma. The control equipment governs the composition of the reagent gas, the flow-rate of the reagent gas, the radio-frequency power, the reactor's operating pressure, and the processing time.

Several gases possess desirable characteristics for plasma cleaning. The specific gas would be determined by the application. An important point to concede is that some surfaces react with some gases directly, a reaction which could actually cause further contamination.

A readily available process gas is necessary. Producing such gases in restricted space may be difficult. Most current cleaning technologies are batch processes. Further design would be necessary to make plasma cleaning a viable line procedure. Once cleaned, precautions must be taken to prevent recontamination. Slight exposure to plastics or other organic substances may allow thin layers of organic compounds to adhere to hyperclean surfaces. This is an important consideration for precision cleaning operations.

Plasma has been used in several different applications for removing (1) organic contamination and residue from substrates, (2) residue from plating baths and washing solutions, (3) conformal coating to repair circuits, and (4) epoxy markings and light oil on automotive bumpers.

3.3.13 Ultraviolet Light/Ozone Cleaning Method

The UV/ozone cleaning process has been used successfully to remove thin organic films from a number of different surfaces, including glass, quartz, mica, sapphire, ceramics, metals, silicon, gallium arsenide, and polyamide cement.

UV/ozone cleaning is a simple process which is relatively inexpensive to set up and operate. Under the proper conditions, the process can produce clean surfaces in less than one minute, and these will remain clean indefinitely during storage under UV/ozone.

The basic UV/ozone cleaning process involves the exposure of a contaminated surface to UV light in the presence of ozone. The cleaning occurs as a result of various photosensitized oxidation processes. Contaminant molecules are excited and/or dissociated by the absorption of short-length UV light. These molecules, and the free radicals produced by dissociation, react with atomic oxygen to form simpler, volatile molecules such as carbon dioxide, water vapour, and nitrogen. This reaction removes the surface contamination.

There are several variables in the UV/ozone process that determine the effectiveness of the cleaning. These include the following: contaminants present, precleaning procedure, UV wavelengths emitted, distance and atmosphere between the UV source and the surface to be cleaned, contact angle of the light, and length of time of the exposure.

Testing must be performed to determine optimal orientations for different contaminants and surfaces to be cleaned. Surfaces that have multiple contaminants, or thick layers of contaminants, require precleaning in order for the UV/ozone process to work. UV/ozone will efficiently clean organic contamination, but particles and inorganic components are more difficult to remove with this process. To maximize the rate of cleaning, the part being cleaned should be kept as close as practicable to the UV light source.

Because the UV/ozone process requires no moving parts, it is easy to maintain and operate. However, both the use of UV light and the presence of excessive ozone can be dangerous to humans. UV light can cause eye injuries and ozone causes respiratory damage. The low workplace limits for ozone (0.1 ppm) require special design considerations.

The UV/ozone process may also cause damage to the surface being cleaned. Staining and discoloration of materials can result from improper wavelengths and exposure times. Overexposure of materials to UV light can also cause corrosion. One positive side effect of the UV/ozone process is the neutralization of static charges on insulator surfaces.

Possible Applications:

The UV/ozone cleaning process has numerous applications. The primary use is substrate cleaning prior to thin film deposition, such as is necessary in the production of quartz crystal resonators. The process is also used for cleaning and storage of metal tools, masks, resonator parts, and storage containers. UV/ozone can be used in a hermetic sealing process that adheres to clean surfaces in an ultra-high vacuum.

Other applications which have been identified include: photoresist removal, the cleaning of vacuum chamber walls, photomasks, silicon wafers, lenses, mirrors, solar panels, complex configured beryllium gyroscope and accelerometer components, and gallium-arsenide wafers.

Future developments in UV/ozone cleaning procedures will come from further testing and experimentation with specific applications. Cleaning techniques need to be refined considerably before this method of cleaning will receive widespread acceptance. The technology advances in plasma cleaning and supercritical fluids may reduce the attention that UV/ozone cleaning will receive, except for use in special medical applications.

3.4 ENVIRONMENTAL AND ENERGY CONSIDERATION

Two major factors in determining the feasibility of any proposed alternative to CFC-113 or 1,1,1-trichloroethane are the environmental impacts and the energy requirements of the substitute. The wide variety of alternative processes available carry with them an equally wide variety of environmental and energy considerations.

Conservation and recovery procedures have proven to be effective in reducing the environmental impacts of industrial solvent usage. These procedures are extremely valuable, not only in cases where acceptable alternatives to CFC-113 and 1,1,1-trichloroethane have not yet been found, but also where organic solvents used in the system vaporize. Currently, though solvent can be recycled, the recycled solvent is rarely used in precision cleaning applications due to its perceived impurities. The solution to this problem is the individual recovery and handling of any solvents in use at a given location. Careful handling will help prevent the mixing of solvents, thereby allowing for treatment and potential reuse. Additionally, companies may purchase small inexpensive solvent reclamation equipment to offset the high costs of solvent disposal.

Several of the alternatives presented in this chapter require wastewater treatment. These alternatives are the aqueous and semi-aqueous cleaning processes. In both cases, the treatment of the wastewater can often be performed in-house so that the water may be recycled.

The ozone-depletion potential (ODP) associated with alternative processes is an extremely important environmental consideration. HCFC solvents have small, but significant, ODPs which may limit their use. Conversely, the ODP of zero associated with alcohols/perfluorocarbons as well as with perfluoroalkanes make them more attractive alternatives. It should be noted, however, that while these two alternatives have an ODP of zero, they both have relatively high greenhouse-warming potential.

Manufacturers of chemical solvents and their HCFC alternative financed a study of the "Total Equivalent Warming Impacts (TEWI)" of the phase out of

CFC-113.[10] TEWI includes the direct effects of emissions of greenhouse gas solvents plus the indirect effects of energy required for supply, operation, and disposal of waste. The analysis aims to include every direct and indirect effect so that alternatives can be compared for environmental acceptability. A summary is presented in Appendix I.

Another important consideration of alternatives to CFC-113 and 1,1,1-trichloroethane in precision cleaning applications is the possible health effect on workers and the general population. Each alternative has occupational hazards associated with its use. For example, aliphatic hydrocarbons are flammable, UV/ozone emits harmful wavelengths of radiation and produces noxious gas, some gases are asphyxiants, and most chlorinated solvents are considered potentially carcinogenic.

While energy considerations are also important in the choice of an alternative precision cleaning method, they usually fall behind environmental impacts in their importance. One case where energy is of major concern is in the plasma cleaning process. In this case, it is a necessity that the process energy be limited to a given level so that the cleaning can be properly performed.

In many of the other processes, the major energy consideration is the amount which is consumed in completing the cleaning process. Extremely high energy utilization will obviously increase the operating costs.

3.5 POTENTIAL GLOBAL REDUCTION OF CFC-113 AND 1,1,1-TRICHLOROETHANE IN PRECISION CLEANING APPLICATIONS

In the first release of this document in 1991, this section was written with the hope that the consortium of academia, industry, and government, could work together to develop alternatives to ozone depleting solvents in precision cleaning. In the 1991 version of this document all of the alternatives that are known in late 1994 were known then. However, in 1994 the industries that were large consumers of ODS have reduced their consumption to approximately one-third of their 1988 usage.

Several of the technologies that were relatively new in 1991 have become more sophisticated in recent years. Supercritical fluid cleaning now has its own society, the Joint Association for the Advancement of Supercritical fluid Technology (JAAST), which is developing and promoting the use of supercritical CO_2 for high reliability cleaning in various applications in the space and defense industry. Semi-aqueous cleaning systems have passed numerous tests and were first used on satellites in 1992. Gas plasma cleaning applications have grown significantly. Organic solvents have progressed from the highly volatile single-component aliphatics (still preferable in some instances) to blends that offer multiple properties. Finally, the PFCs and continuing research on hydrofluorocarbons (HFCs) is moving forward, and new equipment has been manufactured to help reduce the environmental impact of these new solvents.

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[10] AFEAS member companies include Akzo Chemicals BV (The Netherlands), Allied-Signal, Inc. (U.S.), Asahi Glass Co., Ltd. (Japan), Atochem (France), Daikin Industries, Ltd. (Japan), E.I. DuPont De Nemours & Co. (U.S.), Hoechst (Germany), ICI Chemicals and Polymers, Ltd. (U.K.), Kali-Chemie AG (Germany), LaRoche Chemicals, Inc. (U.S.), Montefluous S.p.A. (Italy), and Rhone Poulenc Chemicals/ISC Division (U.K.). The report, produced by Arthur D. Little, is titled Comparison of Global Warming Implications of Cleaning Technologies Using a Systems Approach.

Conservation and recovery, a common theme in 1991, has become commonplace in developed countries. Companies in these countries that are still using ODS solvents have incorporated sliding covers, turn off their heaters at night, and train their workers in proper vapour degreaser operation. By January 1, 1996, the majority of companies in the United States and other industrialised countries, will have met their goal of finding and implementing more environmentally sound cleaning processes.

CHAPTER 4

METAL CLEANING APPLICATIONS

4.1 BACKGROUND

Metal cleaning applications include all applications in which metal parts are cleaned during manufacturing or maintenance except for those metal parts that are included in precision cleaning applications.[1]

Primary Production

Metal cleaning can be divided conveniently into 3 main sub-divisions:

- Primary production
- Periodic maintenance
- Repair and service

Some of the processes which precede metal cleaning include: guillotining stock material, numerically controlled machining from solids, multistage deep drawing, stamping, forging, casting (of all technologies), rolling, extruding, injection moulding, non-destructive testing, welding, and vacuum forming from sheet spinning. The materials which are cleaned in primary procedures include: ferrous metals and alloys; aluminium, titanium, and other light metal alloys; zinc based die cast; other nonferrous metals (e.g., copper and alloys); moulded polypropylene and other thermoplastic materials; carbon fibre reinforced epoxy, glass fibre reinforced epoxy, and other composite materials; and high alumina ceramics.

Finally, the following are examples of processes which follow primary metal cleaning. These procedures include electrolytic surface treatment, painting and application of other coatings, chemical vapour deposition, radio frequency coating, fluid bed coating with polymers, applications of adhesives prior to bonding, galvanizing, simple surface cleaning prior to rework, repair, storage or subsequent assembly, and application of temporary protective materials for storage and delivery protection.

Periodic Maintenance

There are many industrial processes in which plant and machinery are routinely and regularly disassembled, cleaned, reassembled, and refitted with functional materials. This can occur at the end of a working interval (end of shift for example) or at fixed intervals. Many of these require the use of solvents, including CFC-113 and 1,1,1-trichloroethane. Examples include:

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[1] See Chapter 3. Delicate and intricate metal parts that must be cleaned to a degree of micrometer fineness are considered precision cleaning applications in this report.

- Heating, ventilation and air conditioning systems and equipment
- Metal working machinery and equipment
- Hydraulic equipment and systems
- Adhesive spreading machinery (for impact adhesives, adhesives based on polychloroprene), epoxy resins, hot metal systems, etc.
- Silk screen stencils for general printing, solder past printing, etc.
- Instrument pressurized oil filling rigs using Krytox fluorolube and silicone oils
- Polymer forming equipment -- injection moulding, blow moulding -- vacuum moulding, etc.
- Conventional hydrocarbon oil-fill rigs -- transformers, transmission systems -- engines, etc.
- Copiers and laser printing machines
- Newsprint printing machines
- Offset printing machines
- Tooling

Repair and Maintenance

This is possibly the most widespread and diverse subdivision of metal cleaning and covers, for the most part, "cold solvent cleaning" in which 1,1,1-trichloroethane has become the most important cleaning agent in recent years.

To list examples would be to list most mechanical artifacts of the modern world; however, general areas are:

- Primary power sources

    -- auto engines and power trains
    -- truck diesel engines and transmission
    -- marine diesels, auxiliary deck power sources
    -- locomotive diesels and electric motors
    -- aircraft gas turbines and auxiliary power generators

- Industrial handling equipment

    -- conveyor systems
    -- cranes and derricks
    -- mobile overhead hoists
    -- fork lift trucks

- Metal working machinery -- machine tools, press-tools, forging -- deep drawing, etc.

- Sport and leisure

    -- bicycles
    -- boats
    -- outboard motors
    -- cars

-- cameras
-- video recorders
-- television and radio

1,1,1-Trichloroethane is used extensively in metal cleaning. Worldwide production in 1990 amounted to about 726,000 metric tonnes with 66 percent of this total used for metal and precision cleaning. CFC-113 use in metal cleaning is considerably less than 25 percent of that of 1,1,1-trichloroethane. This chapter describes a number of alternative materials and processes that clean metals effectively, including solvent blends, aqueous cleaners, emulsion cleaners, mechanical cleaning, thermal vacuum deoiling, and no-clean alternatives.

4.2 CFC-113 and 1,1,1-TRICHLOROETHANE USE IN METAL CLEANING APPLICATIONS

4.2.1 Metal Cleaning Applications

Metal cleaning is a surface preparation process that removes organic compounds such as oils and greases, particulate matter, and inorganic soils from metal surfaces. Metal cleaning prepares parts for subsequent operations such as further machining and fabrication, electroplating, painting, coating, inspection, assembly, or packaging. Parts may be cleaned multiple times during the manufacturing process.

Metal cleaning usually is done on flat or formed sheet metal or on milled and machined metal stock. Tubing, engine parts, motors, nuts, bolts, screws, honeycomb structures, and rivets are other common configurations. Machined parts tend to have complex and curved surfaces with holes and pockets that can trap both particulate matter and liquids. In large facilities, a wide spectrum of metals and alloys may require cleaning using the same cleaning system. For example, the U.S. Air Force at one location cleans 15 metal alloys during aircraft maintenance operations (Bellar 1988). Metal cleaning also involves the cleaning and preparation of moulds used to cast metal parts, varieties of plastics, and composite materials.

4.2.2 Metal Cleaning Solvents

Traditionally, chlorinated solvents such as trichloroethylene (TCE), 1,1,1-trichloroethane (TCA), perchloroethylene (PCE), and methylene chloride (MC) were used for metal degreasing (ICF 1988). 1,1,1-Trichloroethane began to be substituted for TCE as a metal cleaner in the 1960s; its use, however, increased dramatically because, of all the chlorinated solvents, 1,1,1-trichloroethane has relatively low toxicity, high solvency, low surface tension, and optimum boiling temperature for vapour degreasing. CFC-113 use for metal cleaning began in the 1970s as concerns increased about the toxicity and effects of long-term, low-concentration exposure to some chlorinated solvents. In the United States, the use of CFC-113 as a metal cleaner doubled from 1974 to 1983, from an estimated 26,000 metric tons to 52,000 metric tons.

4.2.3 Metal Cleaning Processes

4.2.3.1 Cold Immersion Cleaning

The most common method of cleaning with ambient temperature solvents is immersion cleaning. Most operations are fairly simple and use halogenated solvents, organic solvents, or blends near room temperature. The basic technique involves immersing or dipping a part by manually, mechanically, or hydraulically lowering the part into a tank containing solvent. While the simplest immersion cleaning method (application) is soaking the article in solvent most soils even if solvent-soluble, require agitation for adequate cleaning. Therefore, immersion/dip cleaning usually is used in conjunction with other operations such as mechanical agitation or ultrasonic cleaning. Immersion cleaning also may be used to remove heavy soils prior to manual cleaning or vapour degreasing. Solvent use in immersion cleaning is relatively high because of drag-out and because there is frequently no vapour level control (condenser, cooling coils) on the equipment.

Mechanical agitation allows nonsoluble particles to be stripped away from the parts, thus producing cleaner parts than a simple dip tank. Mechanical agitation is produced by moving the solvent within the bath or the metal part. The solvent can be agitated mechanically with a motor-driven propeller or a circulating pump, or can be ultrasonically agitated using transducers and an ultrasonic generator. Parts can be agitated by placing them on an agitation platform. Air-agitated dip tanks also improve cleaning efficiency by helping to remove nonsoluble soils, but because this process greatly increases solvent loss by increasing the evaporation losses and might, where relevant, increase concern about the evaporation rate of volatile organic compound (VOC) emissions, it is not a viable option for cleaning enhancement.

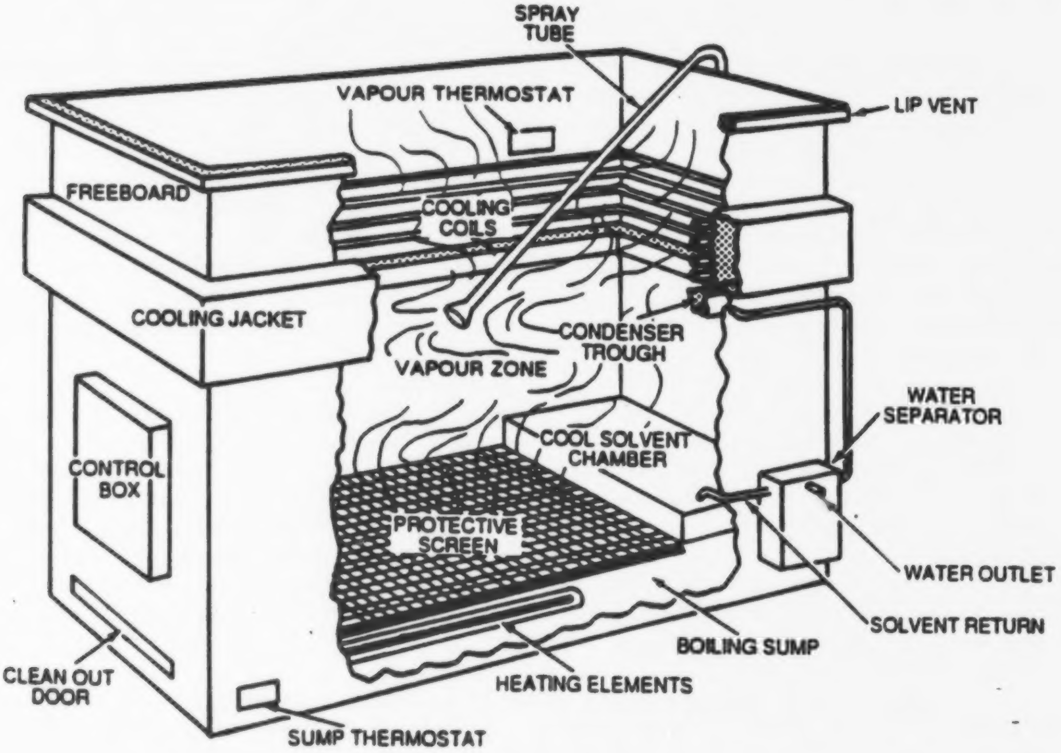
Small containers may be used for maintenance cleaning of electronic parts; large containers may be used for cleaning large machined parts or large volumes of smaller parts in baskets (ICF 1989). Even if the immersion tanks are small, there are often many cleaning stations and the solvent may be changed frequently -- all of which provide additional reasons why cold immersion cleaning uses a relatively large volume of solvent. While many container sizes exist, a typical container (tank) size is about 30 centimetres by 60 centimetres, containing solvent to a depth of 75 centimetres; the working volume of solvent ranges from about 50 to 400 litres (ICF 1989). Tanks are often fitted with recirculation pumps to flush parts. Particulate filters and stills are integrated in some units to maintain solvent quality.

4.2.3.2 Vapour/Hot Liquid Cleaning

Vapour degreasing is a process that uses the hot vapour of a solvent to remove soils, oils, greases, and waxes. A basic vapour degreaser unit is an open-top steel tank with a heat source at the bottom to boil the solvent and a cooling zone near the top to condense the solvent vapours. The vapours displace the lighter air and form a vapour zone above the boiling solvent. The hot vapour is condensed when it reaches the cooling zone by condensing coils or a water jacket, thus maintaining a fixed vapour level. Figure IV-1 is a schematic of a traditional open top vapour degreaser.

Figure IV-1

BASIC VAPOUR DEGREASER - BATCH CLEANING


SPRAY TUBE
VAPOUR THERMOSTAT
LIP VENT
FREEBOARD
COOLING COILS
COOLING JACKET
CONDENSER TROUGH
VAPOUR ZONE
WATER SEPARATOR
COOL SOLVENT CHAMBER
CONTROL BOX
PROTECTIVE SCREEN
WATER OUTLET
SOLVENT RETURN
BOILING SUMP
CLEAN OUT DOOR
HEATING ELEMENTS
SUMP THERMOSTAT

Source: PPG Industries

Parts are cleaned by lowering them into the vapour zone. The temperature differential between the hot vapour and the cool part causes the vapour to condense on the part and dissolve the contaminants. The condensed solvent and contaminants then drip into the boiling solvent. Parts dry quickly upon withdrawal from the vapour zone because they are heated by the solvent vapours and parts remain immersed in the vapour until thermal equilibrium is achieved.

Vapour degreasing is more effective than cold cleaning, where the solvent bath becomes increasingly contaminated. In vapour degreasing, the parts are washed with pure solvent because contaminants removed from the part usually boil at higher temperatures than the solvent and therefore remain in the boiling solvent. Despite the soils contained in the solvent from previously cleaned parts, the boiling solvent produces essentially pure solvent vapours provided that the contaminant level in the boiling sump is kept low. Heavy contamination will contaminate the vapour by upward splashing, as a result of the boiling liquid, or by forming an azeotrope with the solvent.

Metals can be cleaned using one of several batch degreasing methods. These methods are: vapour-only, vapour-spray-vapour, warm liquid-vapour, or boiling liquid-warm liquid-vapour. Modifications to the basic vapour degreaser process are designed to accommodate various cleaning cycles, requirements, or parts configurations. These modifications include spraying or immersing the parts in boiling or cool solvent. Immersion vapour degreasing cycles typically include a warm liquid-vapour cycle and a boiling liquid-warm liquid-vapour cycle. Immersion vapour degreasing is used to clean small parts packed in baskets, to clean the inside of tubing, or to clean intricately patterned parts contaminated with particularly heavy or adherent soil.

Vapour-Only: The simplest degreasing system is the straight vapour method. With this method, solvent vapour condenses directly on the part, dissolves the organic contaminant, and removes it and any particulate residue from the surface of the part by dripping back into the boiling solvent. When the part reaches the vapour temperature, vapour condensation ceases and cleaning is complete. Parts are dry when removed from the tank. Few manufacturers currently make vapour-only units because with the simple addition of a vapour-spray device the effectiveness and applications of the machine are greatly increased.

Vapour-Spray-Vapour: This cleaning method is similar to the vapour-only cycle with the addition of a pure distillate rinse step. In this process, the metal part is lowered into the vapour zone where the condensing solvent cleans the metal. After condensation, the part is sprayed with warm solvent. The spray pressure forces the solvent liquid into holes and helps remove insoluble soils that cannot be removed by vapour alone.[2] The warm spray also lowers the temperature of the metal part. After spraying, the cooled metal part causes further condensation of vapour for the final rinse. This technique also can remove solvent-insoluble soils such as buffing compounds if the part is sprayed immediately upon entering the vapour before the vapour heat can affect the compounds and make them difficult to remove. Vapour-solvent spray-vapour is the most frequently used cleaning cycle (UNEP 1989).

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[2] Spray pressures for standard degreasers should range from 6 psi to 8 psi (40 KPa to 55 KPa) (ASM 1982). Excessive pressure disturbs the vapour zone and causes a high solvent emission rate.

Warm Liquid-Vapour Cycle: During the warm liquid-vapour cycle, the part is held in the vapour zone until condensation stops and then lowered into the warm liquid. Alternatively, parts may be directly lowered into the warm liquid. Mechanical agitation of the warm liquid removes additional soil. The part is transferred from the warm liquid to the vapour zone for a final rinse.

Boiling Liquid-Warm Liquid-Vapour Cycle: This cycle cleans small, intricate parts that are packed closely together in baskets, tubing interiors, or parts with heavy or adherent soil. A part is first held in the vapour zone and then lowered into the boiling liquid. In some processes, the part is lowered directly into the boiling liquid. Once immersed in the boiling solvent, the violent boiling action scrubs off heavy soil deposits, metal chips, and insolubles. Prior to the final vapour phase cleaning, the metal surface temperature of the part is lowered by transferring the part to warm liquid. This method requires large quantities of solvent and is impractical for large parts because of the large volumes of liquid solvent required for immersion.

4.2.3.3 Conveyorized Cleaning

Conveyorized cleaning equipment using 1,1,1-trichloroethane or CFC-113 is generally configured with a spray cleaning stage, immersion in one to three boiling liquid sumps with ultrasonics to enhance cleaning, and in some cases a superheated drying zone. Small degreasing machines using 1,1,1-trichloroethane or CFC-113 may also use ultrasonics to enhance cleaning of small parts and equipment. Vibratory conveyorized machines which move small parts in a screw pattern upward through chlorinated solvent liquid and vapour are still used.

4.2.3.4 Manual Cleaning

Metal surfaces can be hand-wiped with a cloth, brush, or sponge that is moistened with solvent. Solvent containers can be distributed and moved throughout the shop as needed (ICF 1989). Prior to final assembly, and again before painting, aircraft and automobile surfaces, for example, are hand-wiped clean using solvents. Although widely used in assembly plants, manual cleaning is an inefficient method of cleaning parts and does not lend itself to continuous manufacturing operations. It is most appropriate for infrequent maintenance cleaning.

4.2.3.5 Spraying and Flushing Techniques

The effectiveness of spraying and flushing cleaning techniques depends on the solubility of the soil in the selected cleaning media. Spraying and flushing equipment usually consists of a solvent tank, feeder hose, spray gun, overspray containment, and baskets to hold the parts during cleaning. Solvent is usually supplied by a mechanical pump or a compressed air mechanism. These methods are most efficient when cleaning outer metal surfaces. Flushing can clean external and internal part surfaces such as metal castings, tubing, heat exchangers, and assemblies with large cavities.

4.3 ALTERNATIVES FOR REDUCING OR REPLACING CFC-113 AND 1,1,1-TRICHLOROETHANE USE IN METAL CLEANING APPLICATIONS

The control approaches available for metal cleaning operations include solvent conservation and recovery practices and the use of alternative cleaning such as solvent blends, aqueous cleaners, emulsion cleaners, mechanical cleaning, thermal vacuum de-oiling, and no-clean alternatives. Alternatives to CFC-113 and 1,1,1-trichloroethane must be selected and optimized for each application given the varying substrate materials, soils, cleanliness requirements, process specifications, end uses encountered in metal cleaning, and the local environmental, safety, and health requirements. Table IV-1 lists the alternatives that can be used for each process.

4.3.1 Conservation and Recovery Practices

Methods of conserving and recovering CFC-113 and 1,1,1-trichloroethane solvents range from simple procedures for manually removing large contaminants prior to degreasing to adding various filtration apparatuses.

In a poorly maintained plant, only about 20 percent of the purchased solvent quantity is generally recovered. Depending on what measures have already been adopted at a plant, applications of the guidelines summarized in Appendix C can enable total emissions to be reduced by 90 percent. Solvent losses can be reduced from 2-5 kg/h-m^2 of bath area with conventional practice to 0.2 - 0.5 kg/h-m^2 of bath area. For certain alcohol and partially aqueous systems, the overall base rate of annual loss is around 0.03 - 0.05 kg/h-m^2 of bath area.

The recommendations summarized in Appendix C are concerned with the best available technology for the following:

- cold cleaning
- vapour cleaning (including equipment with spray/ultrasound)
- continuous "in-line" cleaning.

4.3.2 Alternative Chlorinated Solvents

The chlorinated solvents that do not destroy the ozone layer, trichloroethylene, perchloroethylene, and methylene chloride (dichloromethane)--also are effective cleaners. Because of their widespread use, they have been extensively scrutinized for their safety, health, and environmental impacts. Many countries have established exposure levels that are considered safe for workers. In addition, many countries have placed additional controls on emissions to the atmosphere from processes using these solvents. Local regulations, Material Safety Data Sheets, and industrial recommendations such as those of the American Conference of Governmental Industrial Hygienists should be used as guidance in establishing safe handling and usage procedures for these solvents.

There are specific metal cleaning operations in which trichloroethylene, perchloroethylene, and methylene chloride are perceived to be the only alternatives to CFC-113 and 1,1,1-trichloroethane. Lack of alternatives can result from concerns about corrosion of the substrate metal (e.g. mild steel), time restrictions between processes (e.g. degreasing as part of a metal heat treating operation), and requirements for removing extremely tenacious soils

Table IV-1. VIABLE ALTERNATIVES TO EXISTING METAL CLEANING PROCESS SOLVENTS

Substitute	Cold Immersion[c]	Hot Immersion[c]	Vapour Degreasing	High Pressure Spray	Manual
Alkaline Cleaners	X	X		X	
Emulsion Cleaners	X	X		X[b]	X
Low Vapour Pressure Solvent Blends[a]	X	X		X[b]	X
Hydrocarbon/Surfactant Blends	X				X
HCFCs	X	X	X		X
Naphtha/Hydrocarbons	X			X[b]	
Naphtha-Terpene Blends	X			X[b]	
Other Chlorinated Solvents	X	X	X	X	X
Steam				X	
Media Blasting				X	

[a] Nonhalogenated mixtures.

[b] With appropriate flammability protection.

[c] Includes agitation such as ultrasonics, mechanical, etc.

Source: Evanoff 1989.

(e.g. asphaltics and waxes) or cleaning intricate parts configurations (e.g. tubes, metal honeycomb). In these special cases, use of trichloroethylene, perchloroethylene, or methylene chloride with the incorporation of the conservation and recovery practices discussed in this report will not only reduce the use of CFC-113 and 1,1,1-trichloroethane, but will also keep use within local regulatory units.

Other compounds that recently have emerged as immersion and wipe cleaning solvents include hydrocarbon/surfactant blends, dibasic acid esters, n-methyl pyrrolidine, volatile methyl siloxanes, and chlorinated aromatics. These products are each tested for performance, toxicity, exposure limits, flammability, carcinogenicity, odour, recyclability, and cost. The U.S. Department of Energy (DOE) and the U.S. Air Force are evaluating these products for toxicity exposure limits, flammability, carcinogenicity, and costs. These products are also being tested for cleaning performance, treatability, recyclability, corrosivity, and VOC emissions. These alternatives may become increasingly available for commercial use over the next five years.

4.3.3 Alternative Solvent Blends

4.3.3.1 Vapour Degreasing

The hydrofluorocarbon (HCFC) blends have ozone-depletion factors associated with them, although these factors are lower than those of CFC-113. HCFC-123 and HCFC-141b have significantly lower boiling points (27-32°C) than CFC-113 (48°C) or 1,1,1-trichloroethane (73°C). This raises the possibility of increased vapour emissions from operating processes, increased fugitive emissions during material transfer, and increased handling and storage requirements. The boiling point of HCFC-225 is 51-56°C, which is equivalent to that of CFC-113. Blends of HCFC-225 therefore could be an alternative to CFC-113. HCFCs should be used with a recovery system in order to prevent solvent emissions, which will minimize worker exposure and protect the global environment (Yamabe 1991).

4.3.3.2 Manual Cleaning

For manual cleaning, a number of commercial solvent blends are available. These products are mixtures of aliphatic and oxygenated hydrocarbon solvents (e.g., ketones, ethers, esters, and alcohols). All degreasing solvents and the organic constituents of blends are volatile and many are flammable. Such solvents or blends may require control measures in accordance with local, regional, or federal regulations or with corporate policies governing their use. These control measures address concerns over environmental, health, and safety issues.

The newer blends being developed are optimised for maximum soil removal, minimum flammability and toxicity, and low composite vapour pressure/evaporation rate. These blends are viable substitutes for 1,1,1-trichloroethane and CFC-113 in situations where volatile organic compounds can be controlled or are not regulated.

4.3.3.3 Cold Immersion Cleaning

Solvent blends of aliphatic naphtha and certain terpenes and dibasic esters are commonly used in immersion cleaning of heavy soils and greases in industrial maintenance operations. These blends are viable substitutes for 1,1,1-trichloroethane and CFC-113 where possible hydrocarbon residue from the high molecular weight fraction of the naphtha does not pose problems and volatile organic compounds can either be controlled or are not regulated. The newer blends being marketed have equal cleaning capacity to those that contain halogenated solvents. These include high flash aliphatic naphthas, blends of aliphatic naphthas with terpenes or esters, and hydrocarbon/surfactant blends.

HCFC-225 is another alternative that has recently become commercially available for use in cold cleaning applications. Figure IV-2 shows the degreasing performance of HCFC-225 compared with that of CFC-113 in cold immersion cleaning. It appears that the degreasing ability of HCFC-225 is comparable to that of CFC-113, thereby making it a suitable alternative.

4.3.4 Aqueous Cleaners

4.3.4.1 Cleaner Formulations

Aqueous cleaners are a viable, broad substitute for CFC-113 and 1,1,1-trichloroethane used in degreasing metals. It is estimated that at least 60 percent of the ozone-depleting solvent degreasing operations for metals could be replaced with aqueous cleaners (Kurita, 1991a). Aqueous cleaners are comprised of three major types of components:

- builders -- alkaline salts such as sodium tripolyphosphate, sodium silicate, or sodium hydroxide which make up the largest fraction of the cleaner.

- surfactants -- organic compounds such as alkyl benzene sulfonates or polyethoxylated high molecular weight alcohols that serve as wetting and emulsifying agents and thus are the principal source of the detersive properties of the cleaner.

- additives -- organic or inorganic compounds such as the ethanolamines or sodium citrate that serve as complexing agents for softening water or binding with undesirable metal ions in solution. Corrosion inhibitors are also added to minimise the effect of the aqueous cleaners on the metal surface.[3] Numerous handbooks and technical references are available and provide a comprehensive explanation of aqueous cleaner chemistry and performance (Linford 1950, Spring 1974, U.S. EPA 1991a).

Alkaline cleaners have been applied successfully in detailed bench and pilot scale testing for metal cleaning applications and, since 1992, in full-scale manufacturing of aerospace components at Boeing, Lockheed, McDonnell

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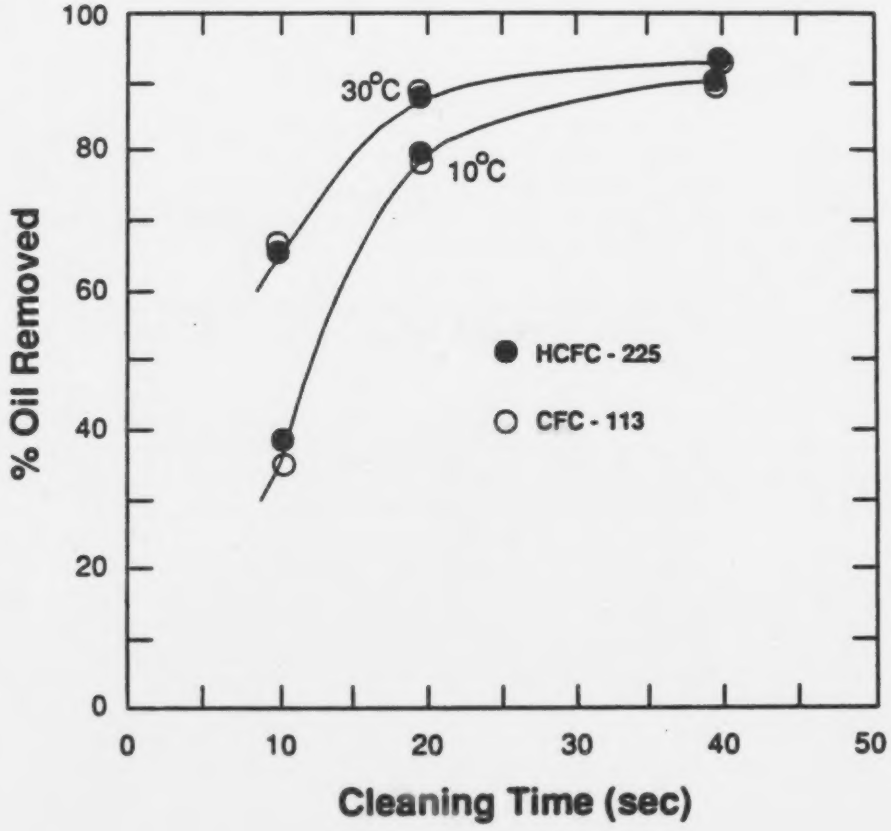
[3] Silicate salts are typical corrosion inhibitors. Other additives include anti-oxidants, such as borates, stabilizers, and small amounts of water-miscible solvents, such as some glycol ethers.

Figure IV-2

DEGREASING PERFORMANCE OF HCFC-225

(Drawing Oil (Houghton Oil))



Douglas, Northrop, and other aerospace and automobile manufacturing facilities(Golden, et.al. 1988, Evanoff 1988, 1994, Suciu 1989). These studies and process changes have demonstrated that alkaline cleaners are effective in situations where a broad spectrum of soils are present and a variety of substrate materials are being cleaned. Hundreds of alkaline cleaning formulations are commercially available and more are currently under development. These products should be screened for specific applications to ensure that they meet the soil removal requirements, are compatible with substrate materials, and do not leave residues harmful to the surface or downstream surface coating processes.

As an alternative to 1,1,1-trichloroethane and CFC-113 use, the U.S. Air Force is specifying the use of Mil-C-87937 Cleaning Compound. A corrosion preventative compound is required if the article is not coated immediately after cleaning. The Air Force is using aqueous cleaning solutions for degreasing of landing gear.

Acidic cleaners[4] are used to remove rust and scale which cannot be removed by organic solvents. They are also used to clean aluminum, a metal susceptible to etching when cleaned with strong alkaline cleaners. In general, acidic cleaners cannot be used as substitutes in organic cleaning applications.

4.3.4.2 Aqueous Cleaning Processes

The principal stages in aqueous cleaning are washing, rinsing, and drying (See Figure IV-3). Soil removal is influenced by thermal (temperature), chemical (concentration), and mechanical (agitation) energies. These can be optimised for specific cases. Mechanical energy in washing and rinsing can be provided through ultrasonics, immersion with agitation of the cleaning solution or of the parts, and spraying. Aqueous cleaning equipment can be characterized as either in-line equipment, used for high throughput cleaning requirements, or batch equipment used for low throughput such as maintenance applications or smaller production processes, or in areas where additional metalworking is required prior to finishing. In-line and batch equipment can be further subdivided into immersion, spray, and ultrasonic equipment. Equipment design features and options vary. Options include solution heaters, dryers, parts handling automation equipment, in-process solution filtration, and solution recycle and treatment equipment. Immersion cleaning, ultrasonic cleaning, and spray cleaning processes are described below.

4.3.4.2.1 Immersion Cleaning

Aqueous immersion cleaning combines chemical, thermal, and mechanical energies. Immersion cleaning consists of four major steps: cleaning, rinsing, drying, and wastewater treatment (recycling or disposal).

In the cleaning process, the parts are immersed in a solution and some form of agitation is added to provide the mechanical energy needed to

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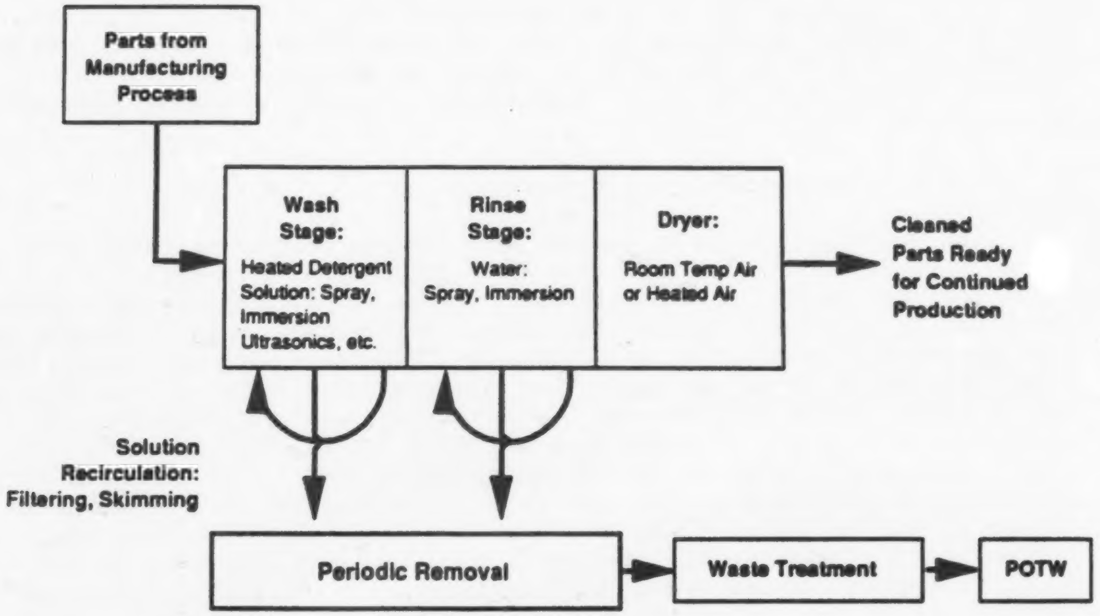
[4] Acidic cleaners contain mineral acids (nitric, sulfuric, phosphoric, and hydrofluoric), chromic acid, or organic acids (acetic and oxalic) plus detergents, chelating agents, and small amounts of water-miscible solvents.

Figure IV-3

CONFIGURATION OF AQUEOUS CLEANING PROCESS


Parts from Manufacturing Process
Wash Stage:
Heated Detergent Solution: Spray, Immersion Ultrasonics, etc.
Rinse Stage:
Water: Spray, Immersion
Dryer:
Room Temp Air or Heated Air
Cleaned Parts Ready for Continued Production
Solution Recirculation: Filtering, Skimming
Periodic Removal
Waste Treatment
POTW

Source: EPA 1989a

displace, dissolve, saponify, and emulsify soils. The cleaned parts are rinsed with deionised or relatively pure water. Additives may be added to enhance wash solution displacement and decrease the amount of water drag-out prior to drying.

Rinsing removes any remaining contaminants and cleaning solution drag-out and may serve as a final finishing step. Rinsing is an essential step in most aqueous cleaning applications. Care should be taken to prevent cleaning fluids from being trapped in holes and capillary spaces. Low surface tension cleaners sometimes penetrate spaces and are not easily displaced by the higher surface tension rinse water. Drying helps prevent surface oxide formation, eliminates potential corrosion caused by solution penetration between close tolerance surfaces, and dries parts for further manufacturing activities.[5] Drying can be a major challenge in aqueous cleaning. In the case of simple geometric or flat surfaces, the challenges may be minimal, but for complex parts, rinsing and drying may require considerable engineering analysis and experimentation. A combination of mechanical methods and multiple operations may be required to displace the cleaning solution from the surfaces of a geometrically complex part. From the perspective of energy or process time, evaporative removal of bulk water is usually not practical. Compact turbine blowers with filtered output can mechanically remove 90 percent or more of the water. Care must be taken to assure desired air quality by appropriate filtration of oil, particulates, and moisture. Noise reduction, humidity, and air conditioning control are other considerations. Conventional convective ovens can be used for drying. For certain lower temperature drying requirements, vacuum dryers can be custom designed and fabricated.

The simplest aqueous immersion cleaning machine configuration consists of a single wash tank. The demands of most cleaning jobs, however, will likely require more complex equipment configurations. If a part must be cleaned to a high degree of cleanliness or if the quality of downstream process solutions is a great concern, several wash and rinse stages would be required.

4.3.4.2.2 Ultrasonic Cleaning

Ultrasonic cleaning effectively cleans intricate parts and contaminants such as carbon and buffing compounds that are difficult to remove (Randall 1988a, Oakite 1988). Ultrasonic machines are appropriate for cleaning small, parts.

Ultrasonic cleaning equipment creates submicron-sized vapour bubbles at the metal surface by vibrating the cleaning solution at extremely high frequencies. As the bubbles form and collapse, they create a scrubbing action that cleans the entire surface of the parts, including blind holes and very small cracks and recesses (Unique Industries 1988). This cavitation process creates extremely high temperatures and turbulence on a microscopic scale. Transducers vibrate the tank (and hence the cleaning solution) at frequencies from 25kHz to 40kHz (Branson 1988).[6]

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[5] Some manufacturing processes require dried parts; others such as many metal finishing process lines (anodizing or electroplating) do not.

[6] 1 kHz equals 1,000 vibrations per second.

Gross contamination of parts may reduce the effectiveness of ultrasonic cleaning. These contaminants are most effectively removed in a heated immersion tank with agitated cleaning solution or in a spray washer (Randall 1988b). Based on research performed by the U.S. Air Force, it has been determined that ultrasonic cleaning enhances the corrosivity of the solvents. Process design requires caution to ensure that the ultrasonics do not cause any metal surface corrosion or damage to the parts. It also uses relatively large amounts of electricity compared to agitation immersion cleaners of similar size (Racquet 1988). Aqueous ultrasonic cleaning equipment can be configured with other cleaning stages featuring parts and/or fluid agitation, or it may be used as one step in a spray machine. The ultrasonic/spray combination is more common for solvent-based equipment than for aqueous equipment.

As an alternative to 1,1,1-trichloroethane vapour degreasing, the U.S. Air Force is recommending the use of dip tank and ultrasonic cleaning procedures utilizing an aqueous cleaner (Kelly AFB).

4.3.4.2.3 Spray Cleaning

Spray equipment cleans parts with a solution sprayed at pressures from as low as 14 kPa to 2758 kPa or more. Depending upon the resilience of the surface to be cleaned, high velocity spray can be used to physically displace soils. In general, the higher the spray pressure, the more mechanical energy is provided in removing soil from metal surfaces. Spray cleaners incorporate low-foaming detergents which are not as chemically energetic as those used in immersion cleaners but are enhanced by the mechanical agitation. Spray cleaning is effective on flat surfaces and those made up of simple geometric parts. Certain configurations such as the interior of an automobile tailpipe, blind holes in machined parts, and other complex geometries have soiled areas that are inaccessible to the sprayed cleaning solution; in these instances, immersion cleaners are more appropriate.

One difference in spray cleaning equipment is the way in which each generates mechanical energy to clean parts. While the mechanical action of spray cleaning equipment is spray action, the mechanical action of an immersion machine may be created by ultrasonic waves, vertical agitation of parts, or bath turbulence. A custom spray machine can combine spray action with the mechanical action used in immersion equipment. Where possible, a high pressure spray is an effective final rinse step. Optimization of nozzle design such as spray pattern, drop size and formation, pressure/velocity, and volume are very important and have a major impact on rinse effectiveness. Spray rinsing uses less water and can provide cleaner surfaces than an immersion bath, since the final water which contacts the part can be quite pure.

The major differences among spray machines, however, relate to the manner in which the parts are handled. Spray washers are of three general types: batch, conveyor, and rotary.

Batch Spray Equipment: Batch spray cleaning equipment consists of a tank to hold the cleaning solution and a spray chamber with a door. Although batch spray machines have a single spray chamber, it is possible to rinse parts in the same chamber by using a separate set of "plumbing" equipment to spray water on the parts. The rinse water is then channelled away from the tank holding the cleaning solution (Kelly 1988). These chambers can be manual or automated.

Batch spray machines can be used for maintenance or manufacturing applications, but generally do not clean as thoroughly as multiple stage machines. Because maintenance applications tend to have lower throughput requirements than manufacturing applications, batch spray machines often are used for maintenance cleaning. For precleaning of heavy soils, large cabinet wash and rinse chambers with spray nozzles located around the perimeter are available and have been designed to accommodate objects as large as electric motors and engines of trains. For removal of heavy greases and tars, high pressure steam is an excellent medium for precleaning and, for some equipment maintenance activities, will provide acceptable cleanliness. This approach has the advantage that the soil and condensate will rapidly separate into water and oil phases, and in most countries neither phase is considered a hazardous waste. Currently Tinker AFB personnel have incorporated an aqueous, biodegradable solvent into their batch spray system to replace 1,1,1-trichloroethane solvents. Results to date have been satisfactory.

Conveyorised Spray Equipment: Conveyorised spray cleaning equipment consists of a tank to hold the cleaning solution, a spray chamber, and a conveyor to feed parts through the machine. A more complex conveyorised system includes multiple wash and/or rinse stages along the conveyor, each stage with its own tank. The rinse water may be recirculated, especially if it contains a treatment chemical such as a rust inhibitor. The rinse water may be discharged if throughput is high or if parts drag significant quantities of cleaning solution out of the wash stages.

Conveyorised equipment is usually used in manufacturing applications with high throughput requirements where parts have flat, even, controlled surfaces. The advantages of conveyorised equipment are high throughput and automated parts handling. If parts are processed before cleaning so that they may be handled automatically from a process conveyor, it may be unnecessary to manually handle the parts during cleaning. Conveyorised spray washers can clean all sizes of parts from a variety of industries. The amount of wash and rinse water required per unit surface area of the part can be as low as 10 percent of that used in batch cleaning. This approach reduces the amount of wastewater generated as compared to immersion cleaning and rinsing. For small parts with uneven and curved surfaces that may not be readily cleaned with immersion and agitation, dishwasher-type units with rotating parts holders and multi-directional spray nozzles are available.

Rotary Spray Equipment: Rotary spray equipment is very similar to conveyorised spray equipment except for the manner in which parts are handled. A rotary machine employs a steel drum with a partition that spirals along the inner surface of the drum such that when the drum is rotating, parts will be transported along the length of the drum. The drum is perforated so the spray can impinge on the parts to be cleaned.

Rotary spray washers are designed to clean small parts such as screw machine parts (e.g., nuts and bolts) and small metal stampings. Rotary equipment can clean large volumes of parts, but the parts must be able to withstand the tumbling action of the rotating drum. Parts with delicate outer diameter threads and polished parts that should not be scratched should be cleaned in a different type of machine using a basket with a locking lid that can hold the parts in place during cleaning (Taylor 1988). High throughput can be achieved with these machines, making them good candidates for high volume manufacturing operations. One tradeoff, however, is that the rotary machines require more energy input than other types of spray machines.

4.3.5 Hydrocarbon/surfactant ("Semi-aqueous" and "Emulsion") Cleaners

Hydrocarbon/surfactant blends are emulsion cleaners that have been developed, tested extensively and are beginning to be used as substitutes for CFC-113 and 1,1,1-trichloroethane in metal cleaning applications which incorporate high viscosity and high molecular weight soils, semi-solid soils, and corrosion sensitive substrates. Hydrocarbon/surfactants are included in many different cleaners and are formulated for different purposes. Examples of these families of chemicals are the terpene hydrocarbons and glycol ethers.

Hydrocarbon/surfactants are used in cleaning processes in two ways. They are either emulsified/diluted in water and applied in a manner similar to standard aqueous cleaners or they are applied in a concentrated form and then rinsed with water. Because both methods use water in the cleaning process, the hydrocarbon/surfactant-based process is commonly referred to as a semi-aqueous process.

The benefits of semi-aqueous cleaning processes include the following:

- Good cleaning ability (especially for heavy grease, tar, waxes, and hard to remove soils)
- Compatibility with most metals and plastics
- Suppressed vapour pressure (especially if used in emulsified form)
- Nonalkalinity of process reduces corrosion potential and reduces the metal content of wastestreams
- Reduced evaporative loss
- Potential decrease in solvent consumption which may lower overall cost
- Ability of some formulas to separate easily from water.

The drawbacks include:

- Recycling or disposal cost of wastewater could make the process less economically viable
- Flammability concerns if concentrated cleaner is used in spray cleaners
- Special equipment designs may be needed to account for flammability
- Objectionable odours with some cleaners, such as terpenes
- VOCs are major components of some cleaners
- Drying equipment will be required in most applications
- Gelling of some cleaners in low water-content emulsions
- Difficulty in reducing surfactants used in cleaners
- Toxicity considerations not yet defined for all cleaners
- Auto-oxidization of some cleaners. For example, d-limonene (a type of terpene) can auto-oxidize. The terpene suffers auto-oxidation naturally from contact with air. This can in some instances be reduced using antioxidant additive
- Semi-aqueous cleaning systems may require more floor space in some instances

- Energy consumption may be higher than that of solvent cleaning systems in applications that require heated rinse and drying stages
- In some applications, high purity water, which is expensive, may be needed.

The steps in a typical semi-aqueous cleaning process are analogous to aqueous cleaning (see Figure IV-4). Equipment for use with semi-aqueous processes are modifications of aqueous cleaning equipment design. In cases where extreme cleanliness is required, hydrocarbon/surfactant cleaning can be followed by a fully aqueous wash step with an alkaline detergent and a deionized water rinse. Application methods that avoid misting such as spin-under immersion or ultrasonics should be used.

Dilute hydrocarbon emulsion cleaners formulated with water may be heated. Less mechanical energy is needed when using a hydrocarbon/surfactant solution than when using an aqueous solution because of the high solvency of hydrocarbon/surfactant cleaners. Rinsing with clean water removes the residues left by the wash step.

Equipment for use specifically with concentrated hydrocarbon/surfactants is available. As with aqueous cleaning, this can be classified as immersion or spray equipment and as either batch or in-line equipment. Because of the solvency of hydrocarbon/surfactants, less mechanical energy is required than in aqueous cleaning to achieve adequate cleanliness. Emulsion cleaners also effectively clean metal parts using ultrasonics.

4.3.6 Mechanical Cleaning

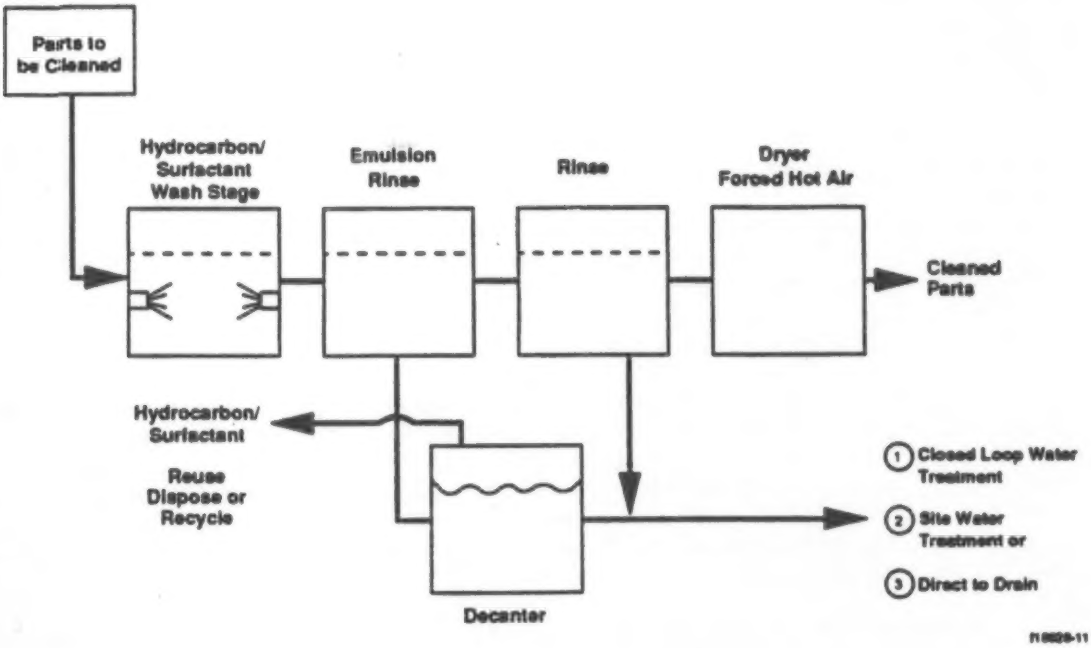
Various mechanical cleaning methods have been used for metal surface preparation and proposed as possible alternatives for CFC-113 and 1,1,1-trichloroethane. Brushing, wiping with rags or sponges, use of sorbent materials, media blasting, and pressurized gases are being investigated to various degrees. These methods, however, are generally best suited for lower grade cleaning requirements or as a precleaning operation in the removal of solid and semi-solid soils.

Pressurized gas may be used in some cases for particulate contamination as an alternative to cleaning with 1,1,1-trichloroethane and CFC-113. Gases which may be used include air, rare earth gases, carbon dioxide, and nitrogen. These gases are readily available in bulk and smaller quantities and in numerous grades of purity. The advantages of cleaning with pressurized gases versus 1,1,1-trichloroethane include the following: low viscosity, low toxicity, high diffusivity, nonflammability, and low capital cost. Disadvantages of using pressurized gas include: low density, high pressure, cleaning of critical components, and often ineffectiveness in cleaning microscopic particles.

Specific technologies under development include wheat starch blasting, sodium bicarbonate blasting, and carbon dioxide (solid) blasting. These methods and others being developed will be evaluated by DOE in collaboration with the U.S. Air Force. Wheat starch can be dissolved in rinse water for disposal and is not considered a hazardous waste after the oils and greases are skimmed off. The carbon dioxide evaporates after cleaning leaving the oil

Figure IV-4

SEMI-AQUEOUS PROCESS FOR IMMISCIBLE HYDROCARBON SOLVENT


Parts to be Cleaned
Hydrocarbon/ Surfactant Wash Stage
Emulsion Rinse
Rinse
Dryer Forced Hot Air
Cleaned Parts
Hydrocarbon/ Surfactant
Reuse Dispose or Recycle
Decanter
① Closed Loop Water Treatment
② Site Water Treatment or
③ Direct to Drain
R8828-11

and grease contaminates behind, thereby reducing the volume of waste generated. Carbon dioxide blasting is currently being used for paint stripping but may be too forceful for less problematic cleaning needs (Kelly AFB).

4.3.7 Thermal Vacuum De-oiling

Thermal vacuum de-oiling is a system that uses a heated vacuum chamber to remove oil from parts by vapourising the oil. The vapours are then pumped through a cold trap where they are condensed and drained from the system for recycle or disposal. Typical cleaning applications for vacuum de-oiling are parts of either simple or complex design that are soiled with low- to mid-viscosity oils. This technology can be used to successfully clean parts following cutting, machining, quenching, and stamping operations. Vacuum de-oiling is also used to clean parts in preparation for brazing, coating, plating, and heat treating operations.

Advantages of vacuum de-oiling include the following: elimination of cleaning solvents, provision of ultraclean parts, simple operation of equipment, reclamation of oils, floor space requirements similar to that of vapour degreaser equipment, and generally no need for environmental permits. The primary disadvantage of vacuum cleaning is that the system is very soil specific. Vacuum cleaning is only capable of removing oils that can be volatilized within certain temperature, time, and pressure ranges. The equipment settings for these variables depend on the characteristics of the oil being removed as well as the mass and surface area of the parts being cleaned. For these reasons vacuum cleaning systems work best in manufacturing applications that have consistent part size and soil loading.

A number of volatile machining oils and forming lubricants are currently available to produce metallic parts without vacuum system or cleaning processes. For example, a heat exchanger of a domestic air-conditioning unit has been made by aluminum fins and copper tubes with many kinds of machining oils and forming lubricants. Traditionally. large amounts of 1,1,1-trichloroethane have been used for removing these oils (Matsui 1991).

4.3.8 No-Clean Alternatives

A number of water-soluble and emulsifiable machining and metal forming lubricants are available. These products are easier to clean using aqueous or semi-aqueous cleaners and are less of a concern for worker exposure. Hot water immersion, spray, or hot water immersion with ultrasonic may be sufficient for removing lubricants that contain emulsifiers. Lubricant spray applicators which discharge a fine well-controlled mist can decrease lubricant usage without affecting product quality. Other alternative lubricants under development include "dry" lubricants and thin polymer sheeting which can be peeled from the surface after the metal forming operation, or in the case of tube forming, "empty tube bending" which accomplishes the forming operation without the use of a lubricant. These products and methods are not standard industrial practices. They do, however, offer the potential for eliminating the need for degreasing.

Material flow through production should also be reassessed to minimise the number of times that a part is degreased and to consolidate the cleaning operations into a centralised unit or location. In many plants, parts are degreased two and possibly three times before finishing and assembly. Consolidation of cleaning operations will decrease the amount of solution treated and waste generated (Evanoff and Weltman 1988).

Segregation and precleaning of heavily soiled parts can extend bath life. Heavily soiled parts can also be routed separately through a single precleaning system; this has the effect of decreasing the amount of contaminated cleaner being generated in the main production area cleaning systems, because the amount of soil entering these systems is minimised (Evanoff and Weltman 1988). Sorbent methods (sorbent laden pads or cloths) can be used to wipe clean parts and surfaces after initial fabrication, thereby reducing the cleaning requirements.

4.3.9 CFC-113 and 1,1,1-Trichloroethane Processes for Which Alternatives are Not Available

Alternatives are currently available for virtually all metal cleaning processes that previously used CFC-113 and 1,1,1-trichloroethane. Those applications for which there is no currently available alternative can be put into two groups. First, there are those applications for which the Parties to the Montreal Protocol have granted an Essential Use Exemption (EUE). In granting these exemptions, the Parties recognize that there are no feasible alternatives to the use of CFC-113 and 1,1,1-trichloroethane in the short term. The second group is comprised of some applications for which stockpiling or recycling of CFC-113 and 1,1,1-trichloroethane is to be used to satisfy short term demand for these solvents.

4.4 COST OF ALTERNATIVES

Due to the wide variety of alternatives available to replace CFC-113 and 1,1,1-trichloroethane in metal cleaning applications, a full discussion of the costs of these alternatives is not practical. However, there are several universal cost components that should be considered when evaluating alternative cleaners or cleaning technologies. These cost components can be split into two groups -- one-time costs and recurring costs.

One-time costs are those costs that are incurred only at the beginning of a project and are not repeated throughout the project life. The most significant of these costs is often the capital investment in new equipment or in the retrofit of existing equipment. Other one-time costs may include items such as laboratory and production testing, environmental, health, and safety impact studies, equipment installation, personnel training, documentation revisions, and environmental permitting.

Recurring costs are primarily operating costs. These costs are incurred throughout the lifetime of the equipment or cleaning process and are often calculated on an annual basis and compared to the costs of the CFC-113 or 1,1,1-trichloroethane cleaning process. Recurring costs may include costs for raw materials (cleaning detergents, solvents, water), energy usage, waste treatment/disposal, and equipment maintenance.

4.5 ENVIRONMENTAL, HEALTH, AND SAFETY CONSIDERATIONS

This document is not a risk assessment and therefore it contains only a general description of some of the environmental health and safety issues associated with each alternative cleaner or cleaning technology. The health and environmental effects of some of these technical options are still being investigated. Certain commercial solvents are generally recognised as toxic while others are suspected but not confirmed as toxic. Other cleaners including aqueous and emulsion cleaners contain constituents which may be hazardous or which can have adverse environmental effects if discharged. Nonetheless, the use of toxic chemicals is permitted in certain cases by governmental authorities but usually require strict workplace controls and effective waste treatment and/or disposal. However, regulations may vary depending on location. In some circumstances it may be prudent to select cleaning options that do not depend as heavily on workplace controls and waste treatment.

The environmental, health, and safety impacts of the alternative compounds that could be used in cleaning applications must be evaluated prior to their use. These impacts may include: acute and chronic health effects, ozone-depletion potential, flammability, aquatic toxicity, global warming potential, and volatile organic compound (VOC) classification. Potential users of alternative cleaners should be aware of the acceptability of a particular alternative in their country, region, and locality. Users should consult local, regional, and federal regulations governing the use, emission, or disposal of any solvent cleaner. Committee members do not endorse the worker safety or environmental acceptability of any of the technical options discussed.

4.6 POTENTIAL GLOBAL REDUCTION OF CFC-113 AND 1,1,1-TRICHLOROETHANE IN METAL CLEANING APPLICATIONS

The Committee consensus is that most CFC-113 and 1,1,1-trichloroethane used in metal cleaning applications can be replaced by these alternatives in accordance with the Montreal Protocol by the year 1996. Some countries, however, are achieving this phaseout according to their own accelerated schedule. Approximately seventy-five percent of the short-term reduction of CFC-113 and 1,1,1-trichloroethane usage is expected to be achieved through aqueous cleaning substitution.

For general degreasing of metal surfaces and parts, aqueous immersion cleaners and solvent emulsions can be substituted for most metal cleaning applications. Many of these substitutions have already taken place in the developed countries and are underway in developing countries. The remaining complex cleaning applications can be replaced by sophisticated aqueous cleaning systems or alternative solvent systems. These complex cleaning applications will require extensive research and design efforts. It is important to allow for the appropriate development time to be sure that inappropriate choices that might have significant health, safety, or environmental impacts, are not made.

More than 60 percent of 1,1,1-trichloroethane was used by small manufacturing companies. The technical and economic impacts are critical to the survival of such companies. They often lack the resources and technical capabilities of larger firms, and essentially must rely on the success of the larger companies to transfer to the smaller firms. This would most likely mean the smaller companies will be about two years behind the larger firms in their phaseout. The critical needs for smaller firms to make the changeovers are: qualification of and transition to new processes, floor space requirements, capital cost, and in many cases water treatment technology.

4.7 SUITABILITY OF ALTERNATIVES FOR DEVELOPING COUNTRIES AND SMALL QUANTITY USERS

Developing countries should be able to closely follow the same scenario as the smaller companies in the developed countries. They may have an additional lag time in their own smaller industries. Each developing country will have somewhat different scenarios depending upon their unique industry basis.

Developing countries which maintain joint ventures with developed countries, or with a strong multinational company-based manufacturing base will be able to incorporate new technology fairly rapidly. Most multinational companies plan to transfer their technology as expediently as possible to their operations in developing countries. However, there will need to be a significant time lag in this technology transfer process as well. It is expected that most multinational companies, including jointly owned affiliate companies should be able to transition their developing country operations within two years of their home operations.

Potential alternatives discussed in this chapter, as well as emerging and developing technologies, will be able to substitute for CFC-113 and 1,1,1-trichloroethane use in all applications, but especially for 1,1,1-trichloroethane in metal cleaning applications. Since more than 60 percent of annual consumption of 1,1,1-trichloroethane has been used by small and medium enterprises (SMEs), both technological and economical impacts are essential. Promotion of technology disclosure and even subsidization could be necessary for average SMEs.

CHAPTER 5

DRY CLEANING INDUSTRY

5.1 BACKGROUND

Dry cleaning enables the cleansing and reuse of fabrics that cannot be cleaned by alternative methods. The inherent environmental friendliness of restoring freshness to soiled articles and garments is matched by extreme efficiency in terms of solvent and energy use in the dry cleaning process itself. Organic solvents are used to clean fabrics because, unlike water, they do not distort some natural and synthetic fibres. Water cleaning of many materials can affect the stability of fabric, lining, and interlining and may cause stretching or shrinkage.

In addition to the actual machine cycle, the term "dry cleaning" includes a large number of operations: customer service, precleaning stain treatment/heavy soil release, post-cleaning stain treatment, tailoring, pressing, and ironing. In such a labour-intensive business, where up to 40 percent of receipts are required for wages alone, dry cleaners have had strong financial incentive to pay close attention to other operating costs, including solvent cost/selling price ratio. Even before the ozone-depletion contribution of solvents became widely known, dry cleaners, for purely commercial reasons, had been frugal solvent users. This scenario has had two other effects: low solvent use/high energy efficiency has been an important factor in the purchase of dry cleaning machines, and manufacturers have competed to produce and market increasingly efficient and environmentally safe products.

For many years, dry cleaning machines have been totally enclosed; incorporating filtration, distillation, and refrigerated recovery systems allows solvents to be continuously recycled. The technology developed by some European dry cleaning machine manufacturers may have applications in the manufacture of metal cleaning machines which require high solvent efficiency.

5.2 CFC-113 AND 1,1,1-TRICHLOROETHANE USE IN THE DRY CLEANING INDUSTRY

CFC-113 is used as a dry cleaning solvent not only because of its low toxicity, stability, nonflammability, and relatively low boiling point, the latter a factor which minimizes energy requirements during the drying and distillation, but also because of its low solvency power (31 Kauri Butanol Value). The low solvency allows the cleaning of fabrics with sensitive dyes and trimmings which may fade or run if cleaned with other solvents. CFC-113 when used in conjunction with leather oils is ideal for cleaning suede and leather garments. As CFC-113 is phased out, however, fashion designers and clothing manufacturers will have less flexibility in their selection and use of fabrics and trimmings and in the future must construct garments that can be dry cleaned in other solvents.

The use of 1,1,1-trichloroethane has been limited as a dry cleaning solvent for a number of reasons. While its high solvency power (Kauri Butanol 124) removes soiling easily and thereby reduces the need for prespotting and recleaning, the solvent damages plastic trimmings, pigment prints, and some bonded fabrics. In addition, the capital cost of the cleaning equipment is approximately 60 percent higher than the cost of CFC-113 cleaning equipment. 1,1,1-Trichloroethane not only has a strong odour, but is also heavily stabilized and, without regular attention, can break down to produce acid which corrodes the machine and possibly ancillary equipment.

Another major factor limiting the use of 1,1,1-trichloroethane in dry cleaning relates to care labelling. The solvents to be used for cleaning are indicated by the marks specified in International Standards Organisation (ISO) 3758. Few garments carry the care label A which indicates the garment may be safely cleaned in 1,1,1-trichloroethane. The majority of garments are marked P (clean in perchloroethylene, CFC-113, or white spirit) or F (clean in CFC-113 or white spirit). If adhered to, these labels protect the dry cleaner from liability if the garment is damaged by the dry cleaning process.

While no more than a few hundred machines in the US and Europe use 1,1,1-trichloroethane as a dry cleaning solvent, a late-1980s study in Japan by Ethane Research Working Group, a group comprised of solvent producers, research and trade associations, machinery manufacturers, and detergent producers, generated interest in machines using 1,1,1-trichloroethane. As a result, some 2,300 machines were in operation by the beginning of the 1990s. However, this number still represented only 4.3 percent of the total machine population.

5.2.1 Dry Cleaning Machines

A modern dry cleaning machine is similar to a combined washing machine/tumbler dryer. The articles are washed in an organic solvent to which a liquid detergent is added during the main wash stage. Following rinsing and spinning, the articles are tumble dried in the same machine. They are only removed after all of the solvent has been recovered. This system, known as a totally enclosed machine or dry-to-dry process, prevents the solvent emissions that previously occurred when clothes were cleaned in one unit and transferred to a separate dryer (transfer machines).

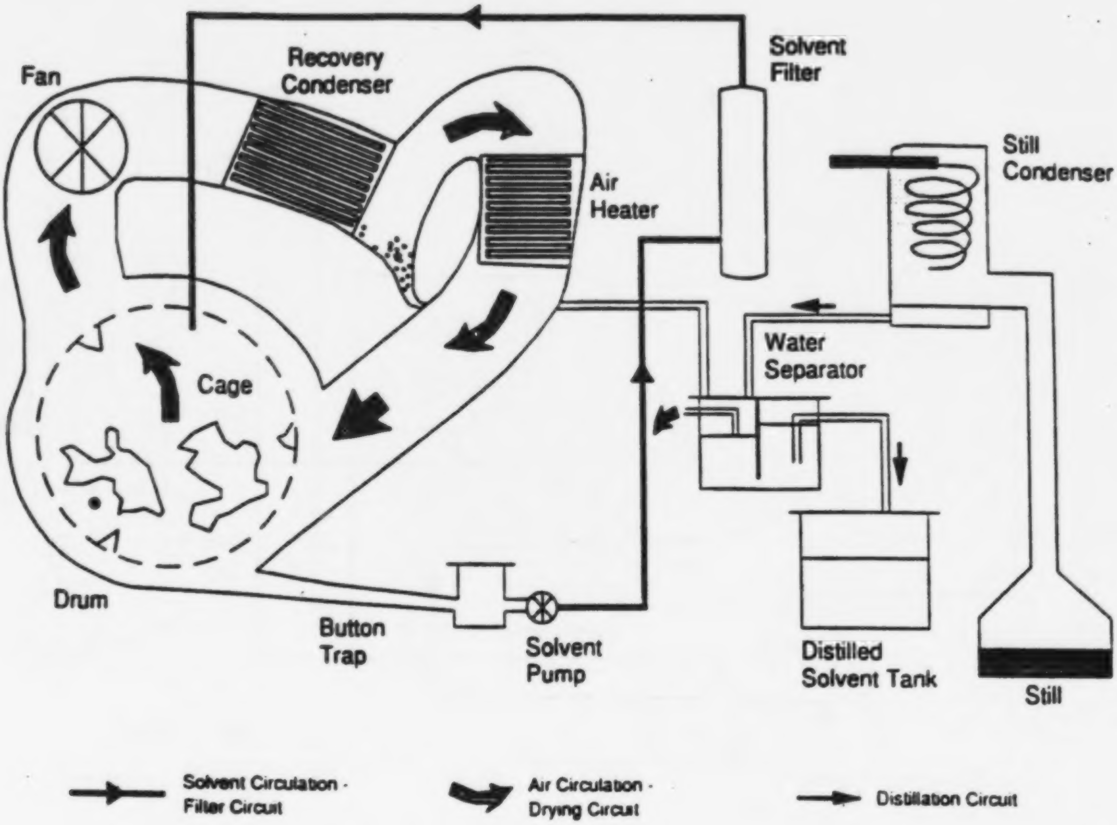
A dry cleaning machine is required to complete three prime functions:

- To thoroughly clean a wide variety of garments and other articles
- To enable complete drying of items before they are taken out of the machine
- To purify the solvent for reuse.

To perform its prime functions, three distinct circuits relating to solvent, air, and distillation operate within the machine. Figure V-1 shows the various flows in a simplified form and Figure V-2 details a typical layout of basic components.

Figure V-1

BASIC DRYCLEANING MACHINE PRINCIPLES


Fan
Recovery Condenser
Solvent Filter
Still Condenser
Air Heater
Water Separator
Cage
Drum
Button Trap
Solvent Pump
Distilled Solvent Tank
Still
Solvent Circulation - Filter Circuit
Air Circulation - Drying Circuit
Distillation Circuit

Shown simplified are the three most important stages in drycleaning machine operation:

- *Solvent circulation - filter circuit (cage, button trap, pump, filter, and back to cage).*
- *Air circulation - drying circuit (cage, fan, recovery condenser, air heater and back to cage).*
- *Distillation circuit (still, still condenser, water separator, distilled solvent tank).*

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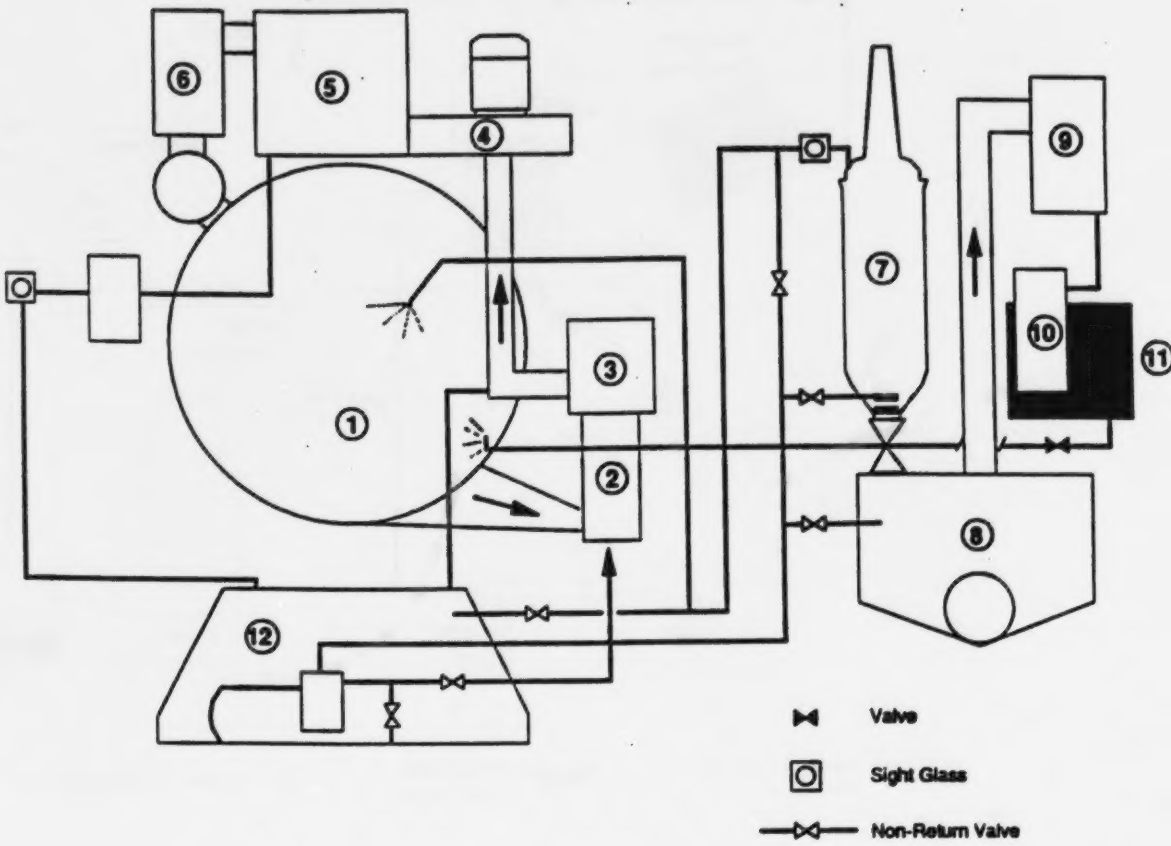
Figure V-2

TYPICAL LAYOUT OF BASIC COMPONENTS


⑥
⑤
④
①
③
②
⑫
⑦
⑨
⑩
⑪
⑧
Valve
Sight Glass
Non-Return Valve

1 *Cage*
2 *Button Trap*
3 *Lint Filter*
4 *Fan*
5 *Recovery Condenser*
6 *Air Heater*
7 *Solvent Filter*
8 *Still*
9 *Still Condenser*
10 *Water Separator*
11 *Distilled Solvent Tank*
12 *Working Tank*

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5.3 ALTERNATIVES FOR REDUCING OR REPLACING CFC-113 AND 1,1,1-TRICHLOROETHANE USE

5.3.1 Conservation and Recovery Practices

Solvent losses in dry cleaning machines result from poor recovery (drying), leakage, distillation losses, and incorrect handling during refilling and servicing. Table V-1 lists some of the reasons for losses from these machines. Improved operator practices and better engineering and controls could conserve much of the CFC-113 and 1,1,1-trichloroethane solvent currently lost. Recycling and recovery technology is already at an advanced stage in which totally enclosed machines feature refrigerated condensation of solvent vapour and activated carbon adsorption of any trace emissions of vapour. Operation and maintenance practices can also ensure that CFC-113 emissions are low. Such practices include activating the drying fan prior to opening maintenance manholes and daily cleaning of the lint filter.

When a machine has not been operated for a number of hours, solvent vapours will fill the machine space. By activating the drying fan prior to opening maintenance manholes, the vapours can be regenerated. Machines can be equipped with a special timing device that activates the drying fan one to two minutes prior to opening the machine door, thereby reducing solvent losses. In general, inspection manholes for the cage (cleaning chamber), button trap, and lint filter should always remain closed during operation and should be opened for the shortest possible interval during servicing. In machines equipped with a button trap that is separate from the regeneration system, special precautions should be taken when cleaning the trap -- all residue from it should be placed in the lint filter for drying.

Efficient operation of the refrigeration unit in dry cleaning machines can reduce CFC-113 losses by up to 25 percent. The large variations in the size of loads processed by machines result in varying quantities of uncondensed vapours being left in the distillation units or machines. Monitoring devices are available to measure the various loads on the refrigeration unit or heat pump and to better control temperatures. All CFC machines can be fitted with a low pressure sensor and regulator for the cooling coils. Such a device monitors the optimal condition for coil operation and switches off the machine when excessive vapour builds up in the expansion vent or when the level of refrigerant is inadequate. When a low pressure device is being installed, the evaporation and condensation temperatures for the refrigeration cell can be adjusted. The suppliers for the respective machines can provide the relevant values for optimum drying efficiency.

Filter replacement significantly reduces solvent losses. A small filter, for example, contains approximately 4 to 5 kg of solvent after drainage. With proper filter replacement techniques, this solvent can be recovered in the cleaning drum of machines. Some machines, however, are equipped with one large filter or many small filters that do not fit the machine drum. Machines with more than four filters can be reconstructed so that filtration takes place only through two filters. Those filters not operating should be put aside for drainage and subsequent regeneration. Machines with a single filter that is too large for the drum can be equipped with sealed drainage vessels that are attached to the machine's regeneration system or stored and transported to a special regeneration facility.

Table V-1. GENERAL SOURCES OF SOLVENT LOSSES FROM DRY CLEANING MACHINES

Leakage at the still door
Leakage at the button trap hatch
Leakage at the lint filter
Leakage at the loading door
Leakage at the lids for the heating and refrigeration chambers
Leakage at the main drive shaft seals
Leakage at the pipe connections
Spillage during refilling
Clogged air-cooled condensers
Substandard maintenance of the lint filter
Inadequate cooling water flow
Solvent in the condensed water
Cleaning of the button trap, especially during operations
Excessive build-up of lint between the outer and inner drums
Negligence during filter replacement or improper machine design
Inadequate final distillation
Overloading
Underloading
Incorrect assembly and installation
Humidity in the cooling system
Incorrect choice of temperatures
Substandard maintenance

A number of daily operation and maintenance activities also can be conducted to reduce solvent losses from CFC-113 and 1,1,1-trichloroethane machines. Because lower air velocity increases drying time, the lint filter should be cleaned or replaced daily. Prior to system start-up, the cooling water circulation system should be checked as well as the refrigeration system, refrigerant, and oil levels. In addition, all seals and gaskets should be checked weekly and adjusted if necessary. The machine should not be overloaded and should be checked to ensure that each load is dried prior to opening the machine.

Other preventive maintenance practices include cleaning the still only when it is cold, ensuring that the temperature of the refrigeration cell does not fall below the freezing point of the solvent, and regularly cleaning the temperature sensors. In addition, the pressure equalization device should be checked to ensure that solvent is not allowed to escape, and the activated carbon filter should be inspected to determine the amount of solvent recovered. Finally, condensed water from the water separator should be collected in a transparent container. Before emptying the container, liquid should be checked for the presence of any free solvent. If solvent is present, it should be separated prior to emptying the container. The contact water should be disposed of in accordance with the appropriate federal, regional, and local regulations.

5.3.2 Alternative Solvents

A number of solvents can be used as alternatives to CFC-113 and 1,1,1-trichloroethane in dry cleaning operations. Table V-2 lists several chemical characteristics of the alternatives discussed below.

5.3.2.1 Perchloroethylene

Perchloroethylene, the most widely used dry cleaning solvent, has been used in this application for over 30 years, during which time the systems for its safe use have become highly developed. For dry cleaners who are seeking to replace their CFC-113 or 1,1,1-trichloroethane machines, perchloroethylene is a logical and practical choice. Its higher solvency power than CFC-113 means that it is not suitable to clean a minority of the fabrics, trims, etc., that can be cleaned in CFC-113 (Clark, 1991b). It is an adequate replacement for 1,1,1-trichloroethane.

Some studies have implicated perchloroethylene as a possible carcinogen although recent toxicological and epidemiological evidence indicates that this is either not proven (EPA 1989b) or due to species differences not relevant to humans (Clark, 1991a). In addition, it is important to bear in mind that modern perchloroethylene machines are extremely efficient and usually result in low solvent emissions. Nonetheless, the use of perchloroethylene in dry cleaning may be regulated in some countries, regions, or localities. For example, the U.S. EPA set national emissions standards for perchloroethylene in September 1993 that apply to both new and existing perchloroethylene dry cleaning facilities. These standards were set in part because perchloroethylene is listed in the Clean Air Act as a hazardous air pollutant, and because a recent study in Staten Island, New York and New Jersey concluded that perchloroethylene is "among the toxic air pollutants found at the highest concentrations in urban air (U.S. EPA, 1993)."

Table V-2. CHEMICAL CHARACTERISTICS OF SELECTED DRY CLEANING SOLVENTS

Solvents	Flamm-ability	Boiling Point (°C)	Heat Required to Boil One Litre[a] (Kcal)	Kauri Butanol Value
CFC-113	NF[b]	47.6	64	31
Perchloroethylene	NF	121.2	116	90
Petroleum-Based Solvents	F[c]	150-210	N/A	26-45
1,1,1-Trichloroethane	NF	74.1	90	124
HCFC-141b	F	32.1	68	58
HCFC-123	NF	27.6	62	60
HCFC-225	NF	51-56	63-66	30-34

[a] Heat required to boil one litre of solvent from 20°C.

[b] NF - Nonflammable.

[c] F - Flammable.

Sources: TSA 1991, Rodgers 1989, Kirk-Othmer 1983, Basu 1989.

5.3.2.2 Petroleum Solvents (White Spirit, Stoddard Solvent, Etc.)

The flammability of petroleum solvents effectively precludes their use in shops, although with proper precautions, they can be a substitute for CFC-113 on many fabrics. In Australia, for example, a fabric labelling convention has been introduced that designates white spirit as a substitute for CFC-113 in the dry cleaning of specific fabrics (Standards Association of Australia, 1987).

Petroleum solvents include white spirit, Stoddard solvent, hydrocarbon solvents, isoparrafins, n-parrafin, etc. Depending on the solvent, characteristics such as flash point, solvency (Kauri Butanol value), distillation temperature, etc. will vary. White spirit and stoddard solvent were developed for dry cleaning applications 40-50 years ago, and have been used to some extent in the U.S., Europe, Japan, and Australia. However, their use has been gradually decreasing over time because of substitutions made to nonflammable solvents and because of regulations restricting emissions of volatile organic compounds. In addition, despite epidemiological studies there are unresolved issues concerning the toxicity of some petroleum solvents.

Recent improvements in dry cleaning equipment to maximize recovery of cleaning solvents while minimizing emissions has resulted in increases in the use of flammable solvents. In addition, new petroleum solvents are being marketed that have lower odour and toxicity.

5.3.2.3 Hydrochlorofluorocarbons (HCFCs)

A number of HCFCs and HCFC blends are currently available commercially for use in solvent applications. These include HCFC-123, HCFC-141b, and HCFC-225. These HCFCs have good stability, excellent solvency, and nonflammability and some HCFCs are suitable for cleaning those delicate fabrics that currently depend on CFC-113. Due to its status as a suspected carcinogen, HCFC-123 is not being marketed for use in solvent applications and is therefore not a possible alternative to CFC-113 and 1,1,1-trichloroethane. In addition, HCFC-141b is not a recommended alternative, especially for 1,1,1-trichloroethane, because it has an ozone depletion potential (ODP) comparable to that of 1,1,1-trichloroethane. HCFC-225, which is a blend of the ca and cb isomers, has a similar boiling point to CFC-113 and is proving suitable for cleaning many sensitive fabrics. Because of dry cleaners' concerns for the solvent cost/selling price ratio, the cost of the blend will determine how readily it is used. It should be noted, however, that HCFCs are transitional alternatives subject to a phaseout under the Montreal Protocol by the year 2030.

5.3.2.4 Other Alternative Solvents

Other classes of chemicals such as iso-paraffins, solvents derived from sugar cane, and hydrocarbon/surfactant blends are theoretically possible alternative dry cleaning solvents. More research, however, is necessary to determine their feasibility for dry cleaning.

Recently, a large chemical manufacturer introduced a synthetic, high-purity hydrocarbon solvent. Some of the properties which may make it a good dry cleaning solvent include good cleaning power, low odour, long service life, high flash point, and low toxicity. A relatively high flash point of 64°C (147°F) provides a greater margin of safety over most other hydrocarbon solvents, thereby reducing building fire suppression requirements in some areas. This solvent is currently in use at dry cleaning facilities and the following properties have been observed (Exxon, 1994):

- compatible with closed-loop, dry-to-dry machines traditionally used with perchloroethylene (PERC) and petroleum solvents
- compatible with common additives
- requires virtually no deodorants since it is virtually odourless
- cycle time comparable to that of a Stoddard solvent and slightly longer than PERC
- little or no plant/building modifications except for the approval from the Fire Marshal
- releases dirt to carbon/clay filters improving cleanliness and prolonging solvent life

Potential users of this or any other flammable solvent should determine their acceptability given local fire regulations.

5.3.2.5 Centralized Processing Facilities

The establishment of centralized cleaning facilities could augment the controls on solvent losses that can be achieved at small, individual dry cleaning establishments. At centralized facilities, additional investments in control devices and standardized operation and maintenance practices can lead to more efficient solvent use.

5.4 COST OF ALTERNATIVES

A dry cleaning machine is the most expensive single item of capital expenditure incurred when establishing a dry cleaning operation. Dry cleaning machines are usually designed to last for 12 to 15 years. Most CFC-113 and 1,1,1-trichloroethane machines can only function using the original solvent. A significant portion of the cost of eliminating CFC-113 or 1,1,1-trichloroethane use can be attributed to the need to replace an otherwise satisfactory dry cleaning machine. The majority of dry cleaning businesses are small and the high capital cost involved in early replacement may result in the businesses being forced to close. For certain CFC-113 machines, one of the HCFCs (e.g., HCFC-225) or HCFC blends discussed in section 5.3.2.3 may prove to be a "drop-in" alternative, thereby saving the cost of early machine replacement. In other CFC-113 machines, extensive and costly (approximately 50 percent of replacement cost) modifications to accommodate an HCFC or HCFC blend may be possible. For machines using 1,1,1-trichloroethane, a modification of the energy balance may allow a change to perchloroethylene. A switch to flammable petroleum or hydrocarbon solvents will require extensive modifications or the purchase of new equipment to provide adequate safety precautions needed because of the flammability of the solvents.

5.5 ENVIRONMENTAL AND ENERGY CONSIDERATIONS

The solvent efficiency of the current generation of hermetically sealed perchloroethylene dry cleaning machines not only reduces emissions but also enables the solvent to be continuously recycled. The machines have introduced a number of features which reduce the amount of solvent being used and which achieve solvent losses of less than one percent of load weight (equivalent to 0.2 to 0.5 $kg/g\text{-}m^2$ of basket cross-sectional area of dry cleaning). Such technology, however, has a significant impact on machine cost, although the initial capital outlay is offset by savings in perchloroethylene, energy, and consumption of cooling water (Clark, 1991a).

These new features include the following systems:

- carbon adsorption
- disc filtration
- heat pump technology
- HCFCs.

Carbon Adsorption

For many years, carbon adsorption systems which adsorb solvent vapour from air prior to discharge into the atmosphere have been available. They have usually been free standing and used in connection with the larger industrial machines. This technology has now been modified to enable adsorption units to be built into smaller machines. Air from the cage at the end of the drying cycle is passed through the adsorption unit prior to opening the cage door for unloading. The cage door can be interlocked to prevent opening until solvent concentration has been reduced to a pre-determined level.

Disc Filtration

This method of removing the insoluble soil from cleaning solvent is gaining much support. When a series of fine (less than 30 micron mesh) polyester disc filters are used, still residues are greatly reduced and the need for filter cartridges is eliminated. This method of filtration, therefore, reduces the amount and cost of waste disposal, eliminates solvent losses associated with the changing of cartridges, and saves the cost of cartridges or other filtration media such as powder.

Heat Pump Technology

With heat pump technology, the heat generated by the warm side of refrigeration units is used to reduce the energy levels required for garment drying and/or to preheat solvent awaiting distillation.

HCFCs

If proven dry cleaning systems for HCFCs or HCFC blends become available, the lower boiling points of these solvents may further reduce energy use. Although the ODPs of HCFCs are lower than those of chlorofluorocarbons (CFCs), they are not zero, and special recovery systems will be needed to minimize solvent emissions.

5.6 POTENTIAL GLOBAL REDUCTION OF CFC-113 AND 1,1,1-TRICHLOROETHANE USE IN THE DRY CLEANING INDUSTRY

Reductions in CFC-113 and 1,1,1-trichloroethane solvent losses from dry cleaning uses are possible to achieve using currently commercially available equipment and cleaners.

Long-term reductions in 1,1,1-trichloroethane and CFC-113 use will occur as the capital stock of machines turns over to new machines that do not use these solvents. Perchloroethylene, in most cases, is the logical replacement, although it is not suitable for cleaning about 5 percent of the fabrics and trims that now can be cleaned with CFC-113.

Proven HCFC systems may emerge in which specialized cleaning requirements can be met. In addition, as the concern over the human health effects of perchloroethylene becomes of greater concern and is addressed by increasingly stringent emissions reduction requirements, other alternatives are likely to gain larger market shares in the dry cleaning industry.

Reductions arising from relocation of 1,1,1-trichloroethane or CFC-113 machines to centralized facilities are unlikely to be significant as it is difficult to justify the large investment required for such a move when viewed against a phaseout schedule. The solvent reduction benefits from centralized facilities may be more fully realized with perchloroethylene or the other alternatives described as companies replace machines using CFC-113 and 1,1,1-trichloroethane.

The Committee consensus is that no CFC-113 or 1,1,1-trichloroethane should be necessary in the dry cleaning industry in developed countries by the year 1996. CFC-113 and 1,1,1-trichloroethane use can be largely eliminated through the use of currently available alternative solvents, such as perchloroethylene. Furthermore, the Committee warns garment manufacturers that clothing or other textile products that can only be cleaned in CFC-113 may, at some future date, no longer be able to be cleaned. As a precaution, in the event that HCFC substitutes do not become available, garment manufacturers are advised to ensure that fabrics, trimmings, and interlinings are suitable for dry cleaning in perchloroethylene.

CHAPTER 6

ADHESIVES APPLICATIONS

6.1 BACKGROUND

1,1,1-Trichloroethane is used as an adhesive solvent because it is non-flammable, dries rapidly, does not contribute to local air pollution, and performs well in many applications, particularly foam bonding. The use of 1,1,1-trichloroethane in these applications has diminished due to the implementation of the Montreal Protocol. However, in 1989 40-50 thousand tonnes of the chemical were used in adhesive applications in the U.S., Western Europe, and Japan (Chem Systems, 1989). As CFC-113 is not used in adhesives it is not discussed further in this section.

A partial list of applications where 1,1,1-trichloroethane adhesives are used includes:

- packaging;
- non-rigid bonding;
- construction;
- tapes;
- rigid bonding;
- transportation; and
- consumer adhesives.

This section provides a summary of 1,1,1-trichloroethane use in adhesives. Section 6.2 discusses the physical properties of 1,1,1-trichloroethane that make it attractive for adhesives use and gives examples of its use. Section 6.3 discusses a number of alternatives for reducing or replacing 1,1,1-trichloroethane in adhesives, and Section 6.4 compares the costs of these alternatives. Section 6.5 discusses the environmental and energy considerations of alternatives. Section 6.6 presents potential global reduction of 1,1,1-trichloroethane in the adhesives industry. Finally, Section 6.7 discusses the suitability of alternatives for developing countries and small quantity users.

6.2 1,1,1-TRICHLOROETHANE USE IN ADHESIVES APPLICATIONS

1,1,1-trichloroethane has several physical characteristics that provide desirable performance properties for adhesive applications. It has been used for many years in contact bond adhesives because it offers similar performance characteristics to the flammable solvent-based adhesives it replaced and yet is not flammable. In particular, it has found wide use in bonding decorative laminates to substrates such as particle board and plywood (Dawnkaski 1991). In general, 1,1,1-trichloroethane has been used when:

- a solvent-based adhesive is desired for rapid drying time and high film strength, and either flammability is a consideration or the use of volatile organic compounds (VOCs) is restricted; and

- bonding certain substrates, such as foam, plastic, or wood.

Table VI-1 presents physical properties of 1,1,1-trichloroethane and selected conventional solvents used in adhesives. Of particular note is that 1,1,1-trichloroethane (and methylene chloride) has no flash point.[1] The other conventional solvents listed in the table have low flash points, low explosion limits, and are considered to be flammable solvents.

1,1,1-trichloroethane also displays low water affinity. Only 0.05 grams of 1,1,1-trichloroethane can be dissolved in 100 grams of water at 25°C. It is, therefore, used as a coalescent in some water-based adhesive systems. 1,1,1-trichloroethane evaporates faster than other solvents used in adhesive formulations, which allows increased throughput in applications where drying time contributes to the overall process yield (e.g., in pressure-sensitive tape manufacturing). The density of chlorinated solvents, such as 1,1,1-trichloroethane, is greater than that of conventional solvents used in adhesives, and the solids/viscosity relationship of adhesives diluted with chlorinated solvents is different from those diluted with conventional solvents. When selecting solvent alternatives, these differences are taken into account with regard to application cylinders, machine speeds, and so on.

1,1,1-trichloroethane has a mid-range solvency when compared to conventional adhesive solvents. The chemical is an active solvent for alkyl, acrylic, chlorinated rubbers and many phenolic resins and a diluent for nitrocellulose, vinyl, and epoxy resins (Dow 1984). 1,1,1-Trichloroethane can be mixed with other solvents to adapt its solubility strength to the needs of a specific resin system. This task is usually performed by the adhesive formulator who customises solvent blends to meet specific solubility needs.

In the U.S., 1,1,1-trichloroethane is exempt from volatile organic compound (VOC) regulations in most states, which provided an incentive for some adhesive manufacturers and their customers to use the solvent in place of VOC solvents (Dawnkaski 1991). As an example, 1,1,1-trichloroethane has been used as a replacement for organic solvents in the following applications (UNEP 1989):

- manufacture of styrene-butadiene latex adhesives;
- formulation of polyurethane adhesives;
- replacing extremely flammable solvents in pressure-sensitive tapes and labels, and in industrial and consumer adhesives;
- substituting flammable solvents in PVC flooring adhesives; and
- replacing ethyl acetate solvents in laminating adhesives used in packaging.

In general, 1,1,1-trichloroethane is used as active solvent in solvent-borne adhesives and as a diluent in water-borne adhesives. Solvent borne adhesives containing 1,1,1-trichloroethane are primarily contact adhesives and

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[1] Flash point temperature is the lowest temperature at which vapours above a volatile combustible substance ignite in air when exposed to flame.

Table VI-1. PHYSICAL PROPERTIES OF COMMON ADHESIVE SOLVENTS

Solvent	Flash Point Open Cup (°C)	Flammable Limit in Air 25°C (Volume %) Upper	Lower	Water Soluble in 100g Solvent (g)	Kg/ Liter 20°C
1,1,1-Trichloroethane	NF[a]	12.5	7.5	0.05	1.314
Methylene Chloride	NF	22.0	14.0	0.17	1.316
Toluene	7.22	7.0	1.3	0.05	0.870
n-Hexane	-27.8	6.9	1.25	0.01	0.678
Methyl Ethyl Ketone	-5.6	11.5	1.81	11.80	0.804
Ethyl Acetate	-2.2	11.0	2.25	3.3	0.900

[a] NF = No Flash Point.

Source: Dow 1984.

spray adhesives used where good "green bond," or initial bond, is desired, as in the manufacture of foam cushioned furniture or plastic laminated countertops. The primary binders in these adhesives are rubbers of various kinds, including natural rubber, neoprene, chloroprene, and styrene-butadiene rubber. Acrylic binders are also used. Adhesive grades applied by extrusion or spraying have dry solids contents of less than 15 percent, while other grades are between 15 and 30 percent. Table VI-2 shows specific binding substances (i.e., adhesive type) where 1,1,1-trichloroethane is used.

In assembling foam padded furniture, for example, a thin film of adhesive is applied to the two surfaces being joined. When the foam padding is applied to the frame, the adhesive bonds immediately. The adhesive joint must then hold without adhesive or solvent migrating into the foam material and ruining it. In other words, the tack, or "stickiness", of the adhesive must decline quickly. The time between application and the last moment for assembly (when the tack disappears) is called the "open assembly time". The solvent-based rubber adhesives have good properties in these respects, with good green bond and a short open assembly time.

Two paths are available for solvent reduction in adhesives; established technologies and emerging technologies. Established technologies include other solvent-based adhesives, water-based adhesives, hot melt systems, and solvent recovery systems in continuous operations. Emerging technologies include radiation cured adhesives, "high solids" adhesives, powders, and reactive liquids. These technologies are discussed in further detail below.

6.3 ALTERNATIVES FOR REDUCING OR REPLACING 1,1,1-TRICHLOROETHANE USE

6.3.1 Other Solvent-Based Adhesives

The rubber binders used in 1,1,1-trichloroethane adhesives are soluble in other solvents, such as acetone, ethyl acetate, heptane, and toluene. Although there has been a general trend in the U.S. and Western European adhesives industries to replace organic solvent-based adhesives with solvent-free types, one alternative is to return to earlier solvent formulations. According to one market survey conducted in the U.S., volatile organic compound (VOC) regulations provided the initial impetus for moving away from solvent-based technologies. However, for some industry sectors, such as tapes, this shift would continue in the absence of regulations because alternative technologies are more competitive on a cost and performance basis (Ellerhorst 1982). The use of solvent-diluted (as opposed to solvent-based) adhesives has also been declining for economic reasons (Kimel 1988).

The use of solvent-based adhesives is costly because they require flame proof equipment and extraction systems (O'Driscoll 1988, Johnson 1991). The premises and apparatus must be designed fire-safe in terms of both sparking and static electricity. In many cases it is necessary to use robots in closed booths, which means large-scale use is required for cost effectiveness.

Table VI-2. USES OF 1,1,1-TRICHLOROETHANE

Use Sector	Binding Substance
As Active Solvent in Solvent-Borne Adhesives	Styrene-Butadiene Rubber (SBR) Neoprene Natural Rubber Rubber Cement Other
As a Diluent or Coalescent in Water-Borne Adhesives[a]	

[a] No data is currently available on the specific binding systems that employ 1,1,1-trichloroethane as a diluent and or coalescent.

Source: Based on Skeist 1987.

6.3.2 Water-Based Adhesives

Some adhesives use water, in lieu of organic solvents, as the primary solvent. A water-based adhesive can be a solution, a latex, or an emulsion. Solutions are made from materials that are soluble in neutral or alkaline water; most natural adhesives are water solutions. Latexes are stable dispersions of solid polymeric material in an essentially aqueous medium (Landrock 1985), while emulsions are stable dispersions of immiscible liquids. Emulsions usually appear milky white in the liquid state but dry to a clear film. In industry, the terms latex and emulsion are generally synonymous. Latex adhesives are more likely to replace solvent-based adhesives than solution adhesives because their synthetic binders provide more versatility and higher performance (Landrock 1985). Latexes, however, require more extensive formulation because they are produced from polymers not originally designed for use as adhesives.

The binding substances that are candidates for water-borne adhesives include: natural substances, including natural rubber; synthetic elastomers such as styrene butadiene rubber, neoprene, and isoprene; vinyl resins such as polyvinyl acetate (PVAc) and polyvinyl chloride (PVC); acrylics; and epoxies (Landrock 1985). Some of these binding substances require additional formulation and additives like emulsifiers, surfactants, or additional resins. Water-based binding substances use the traditional methods for adhesive application. These include brush, spray, roll coat, curtain, flow, and knife coat (Landrock 1985).

Recent literature on water-based adhesives suggests that there is still much debate about the overall effectiveness of water-based adhesives for many end uses. In general, water-based adhesives show good durability, water resistance, and adhesion to a wide variety of substrates, especially in the area of nonporous to porous bonding (Chao and Hernisch 1986). Problems still exist in the bonding of non-porous to non-porous substrates because water is difficult to evaporate from such substrates. In addition water-based adhesives are not suitable for non-structural bonding of rubbers and many plastics.

Water-based adhesives can bond moist surfaces better than solvent-based adhesives. One inherent advantage of water emulsions is that viscosity is independent of molecular weight of the resin (Fries 1984). The higher initial molecular weight polymer provides greater internal cohesive strength to the freshly made bond. This initial, green bond is important to avoid uneven bond stress and blisters in laminating applications (Fries 1981 and Fries 1984). Poor initial bond strength has been a criticism of low molecular weight water-borne adhesives. Unlike solvent-borne and hot melt adhesives, there are no restrictions on the initial molecular weight of the resin for water emulsions.

The direct replacement of solvents by water is not feasible in all sectors. Selecting water as the vehicle in adhesives demands totally new concepts in raw materials and formulation as discussed above. Water-based adhesives often require special handling in manufacturing, storage, and application. They must be kept from freezing during shipment and storage (Landrock 1985, Dawnkaski 1991). Problems with corrosion require that all storage and transfer pipes be corrosion-resistant. Some manufacturers, however, maintain that corrosion is not a factor if additives which prevent corrosion are included in the formulation, and one set of laboratory tests found water-borne adhesives not to be more prone to corrosion than solvent-borne adhesives (Manino 1981). The problem has not been resolved conclusively; more research and development is needed in this area (Johnson 1991). Another problem with storing water-based adhesives is that agitation is needed to maintain consistency of the dispersed materials in the adhesive solution. Yet agitation can cause foaming, and anti-foaming agents compromise adhesive bond performance.

Water-based adhesives reportedly have other performance disadvantages when compared with solvent-based adhesives. During application, water-based adhesives do not "wet" surfaces as well as their solvent-based counterparts due to water's inherent polarity and high surface tension (Dawnkaski 1991). Minor contamination of the surface (e.g., oil, mould release, fingerprints) can lead to bonding problems.[2] Water-based adhesives do not have the versatility of application provided by solvent-based adhesives (Johnson 1991). Although polar substrates, such as natural rubber, bond well with water-borne adhesives, nonpolar elastomer substrates, such as ethylene propylene copolymers, are difficult to bond (Manino 1981). Silicones and fluoroelastomers provide a greater challenge, and water-borne adhesives still cannot compete with solvent-borne systems in these areas (Manino 1981). Finally, spray application of water-based adhesives can be especially difficult due to the ease with which water- carried adhesives are atomized. Spray application results in a fine mist that can travel to all areas of a shop, coating persons and objects with a thin coating of adhesive (Dawnkaski 1991).

6.3.3 Hot Melt Adhesives

The Committee D-14 of the American Society for Testing and Materials (ASTM) defines a hot melt adhesive as one that is applied in a molten state and forms a bond upon cooling to a solid state (Fullhart and Mottershead 1980). Hot melts are primarily 100 percent solids thermoplastic bonding materials that achieve a solid state and resultant strength upon cooling. The major applications of hot melt adhesives are bookbinding, packaging, textiles, and product assembly, including construction glazing and automotive door panel and carpet installation (Fullhart and Mottershead 1980). Application methods include melt-reservoir and pressure-feed systems (Landrock 1985). The binding substances that provide the foundation for hot melt adhesives are ethylene vinyl acetate (EVAc) and other polyolefin resins; polyamide (or nylon) and polyester resins; polyester/amide resin alloys; and thermoplastic elastomers (Landrock 1985). Foamable hot melts (e.g., polyethylene) form a superior bond with metals, plastics and paper (Landrock 1985).

Although earlier hot melt pressure sensitive adhesives (PSAs) had unacceptable colour retention and UV resistance, present hot melt PSAs are clear and UV resistant (Maletsky and Villa 1984). Hot melt PSAs now compete with water-based acrylics in outdoor applications (Maletsky and Villa 1984). They have been used on paper labels for indoor applications since 1978.

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[2] A solvent-based primer can boost performance by ensuring a clean substrate for the water-based adhesive. A primer uses less than half as much solvent as solvent-borne adhesives. 1,1,1-Trichloroethane has been used as a primer to degrease many substrates (Landrock 1985).

Hot melts are, however, limited in several key performance characteristics. They have poor specific adhesion to a number of substrates, creep under load over time and at high temperatures, have limited strength, and limited heat resistance (Landrock 1985). A specific hot melt acrylic used for pressure-sensitive applications has poor tack for many applications (Lipiec 1982). Room temperature shear resistance and elevated temperature shear resistance are also deficient in hot melt acrylic PSAs (Lipiec 1982).

6.3.4 Radiation Cured Adhesives

Radiation curing is a production technique for drying and curing adhesives through the use of radiant energy such as ultraviolet (UV), infrared (IR), electron beam (EB), gamma, and x-rays. In essence, radiant energy becomes chemical energy in the forming of the adhesive bond. The binding agents that can be cured with radiant energy are acrylics, epoxies, urethanes, anaerobic adhesives, and polyester resins (Adhesives Age 1988). Pressure-sensitive or 100 percent non-volatile formulations of adhesives are applied by conventional techniques between one or two plastic films and then cured by exposure to radiant energy (Chemical Week 1987). Application areas include electronics, communications, consumer products, transportation, packaging, and medical and dental uses (Bluestein 1982). Radiation cured adhesives are especially well adapted for pressure sensitive tapes. One drawback is that adhesive curing is only possible in the "line of sight" of the radiant energy. Pressure-sensitive tapes are another major application of radiation cured adhesives. High growth is anticipated for UV and EB cured adhesives. It is not evident whether UV methods are particularly suited to bonding opaque substrates.

6.3.5 High Solids Adhesives

One way to lower volatile organic compound (VOC) emissions when using solvent-based adhesives is to increase the percent solids in the formulation. In the specific example of polyester urethane laminating adhesives, high solids/low solvent adhesives are an alternative to solvent-borne adhesive systems. Using the existing technology for polyesters and polyester urethane systems, high solids have been very successful in laminating uses (Bentley 1983). One manufacturer supplies a 68.5 percent solids polyester urethane laminating adhesive which meets VOC regulations by lowering the amount of solvent used (Wood 1984). High solids adhesives have good performance characteristics, including initial bond strength, comparable to that of 30 percent solids adhesives in medium and high demand applications and can be applied using existing equipment at normal line speeds with minor modifications (Wood 1984).

In other application areas, such as bonding rubber assemblies, high solids adhesives have not been as successful. For bonding rubber assemblies, high solids adhesive films are too thick, which results in limited versatility and generally poor performance (Manino 1981). In general, high solids adhesives cost more per pound since they do not contain the nonreactive solvent as a diluent. However, advanced products consisting of a 100 percent solid adhesive and a liquid primer are now commonly used in critical structural bonding applications, such as aircraft wings. The 100 percent solids structural adhesives generally require refrigeration, shelf life control, and training or practice in application.

6.3.6 Powders

One-part epoxies, urethanes, and natural resins are often supplied as powders that require heat to cure (Frisch and Xiao 1988). Powders are only used for non-pressure-sensitive applications. They are generally applied in three ways: by sifting the powder onto pre-heated substrates, by dipping a preheated substrate into the powder, and by melting the powder into a paste or liquid and applying it by conventional means (Landrock 1985). One advantage of the powder form is that no mixing or metering is necessary. However, powders must be refrigerated to maximise shelf life (Landrock 1985). No data are currently available comparing performance and cost with solvent-borne adhesives.

6.3.7 Non-Volatile Solids and Liquids and Reactive Liquids

Moisture cure adhesives and reactive liquids can be applied as 100 percent non-volatile solid and liquid systems. These adhesives are composed entirely of binding substances, modifiers, and fillers (i.e., they have no carrier or solvent). Moisture cure adhesives cure upon exposure to the humidity in the ambient air; this type of adhesive requires application in a humid environment and might not work well in dry climates. Moisture cure adhesives are available in 100 percent non-volatile liquids and solids, hot melts, solvent-borne formulations, and other technologies (Frisch and Xiao 1988). Moisture-cured silicone-based adhesives include at least two specific types, methoxy-cured and acetoxy-cured. These systems use water in the atmosphere to react in the adhesive reaction. The by-products are small quantities of either methanol or acetic acid.

The 100 percent non-volatile moisture cure systems are of interest because they offer another alternative to the solvent-based systems. The two primary binding substances used in moisture cure adhesives are isocyanates and polyurethanes (D'Autilio 1983). They are available as single and multiple component adhesives. The two-part system physically separates the binding agent from the curing agent during storage. Although the adhesive requires metering and mixing to cure, the two-part system has a longer shelf life. The two-component system also achieves higher performance. A two-component solvent-free isocyanate adhesive that does not require moisture to cure nor precise metering has appeared on the market. A thin coat of one component is applied to one part and a thin coat of the other to the second part. The two are brought together and form a rapid and strong bond in a few seconds. As the bond does not require oxygen to form (i.e., is anaerobic), isocyanate adhesives are useful for joining metallic and other non-porous parts. Tests have shown, however, that the electrical properties of the adhesive exclude it from electronics applications, such as bonding surface mounted components to substrates prior to wave soldering.

Some two-component adhesives use reactive solvents which form part of the cured mass and thus do not depend on evaporation. In use, one solution consisting of an elastomer colloidally dispersed in a monomer is cured by a second solution through a free radical chemical polymerisation, thereby creating the bond (Prane 1980). The binding substances for reactive liquid adhesive systems include epoxies, urethanes, polyesters, silicones, polysulphides, acrylics, modified phenolics, and resin compounds (Prane 1980). Reactive liquids are used for high performance structural applications. Application methods are similar to those used in contact adhesives, namely, brush, roller, or spray (Prane 1980). No information is currently available on the relative performance attributes of this emerging technology.

6.4 COSTS OF ALTERNATIVES

Substitution costs for the established alternative technologies are in most cases driven by the raw material costs and capital investments required to implement these technologies. Research and development resources are also required to develop and test alternative technologies - water-based adhesives, hot melt adhesives, and solvent recovery - for specific adhesive systems. The cost of switching to an alternative solvent is highly dependent on whether or not the solvent is a VOC since VOC emission and worker safety regulations may require installing expensive ventilation and vapour recovery equipment.

Converting to water-based solvents allows adhesives users to reduce their inventory of solvents. Water-based adhesives require stainless steel application equipment, hoses, stirrers, etc., and there may be significant conversion costs. Water-based adhesives clean easily during application, but the rinse water should be properly disposed of or recycled.

Although hot melt adhesives are more expensive per unit of formulated weight, in many applications their use leads to reduced overall costs. The conversion to a hot melt system requires installing new, moderately expensive equipment. The capital costs of conversions are offset by saving space and energy from the use of automated equipment, lowered raw material costs, and increased productivity (Lipiec 1982). Hot melts can be applied faster and more efficiently than water-based adhesives because there is no delay for evaporation (Kimel 1988). Since hot melt formulations contain 100 percent solids, they can be slightly more expensive when shipment in refrigerated trucks is required.

Prior to curing, radiation cured adhesives have a longer shelf life than most adhesives (Bluestein 1982). Their use leads to production of a more reliable product, lower rejection rates and labour costs, and reduced cleanup and inspection times (Moreau 1988). Radiation cured adhesives are an option for new production facilities due to the simpler, space-saving equipment (Bluestein 1982). Among the radiation curable technologies, UV and EB curing have separate applications. UV curing is more cost effective for smaller applications, whereas EB curing is better adapted for large scale operations.

Radiation cured adhesives have some disadvantages. Existing equipment cannot be used for this type of adhesive without the addition of a cure unit (Bluestein 1982). In addition, the applications are limited to "line of sight" for radiation cured adhesives.

As mentioned above, high solids adhesives typically cost more but outperform their solvent-borne counterparts at lower solids levels. This technology development is ongoing.

6.5 ENVIRONMENTAL AND ENERGY CONSIDERATIONS

There are a number of environmental and energy implications to replacing 1,1,1-trichloroethane-based adhesives with alternatives. Returning to the use of other solvent-based adhesives will affect local air pollution and worker safety unless precautions are taken. VOC solvents contribute to the formation of tropospheric ozone and their use is restricted in many localities; their flammability requires the installation of special equipment to minimize the danger from fire or explosion. These concerns were the incentive to move to the use of 1,1,1-trichloroethane initially.

Water-based adhesives have a number of characteristics that make them attractive substitutes. As they contain no volatile organic solvents, water-based adhesives do not contribute to local smog problems and are nonflammable. They can, however, emit small quantities of hydrocarbons, ammonia, and emulsion-stabilising substances. In ideal situations, these pollutants can be removed to some extent using, for example, wet scrubbers.

From the energy perspective, drying ovens used for solvent-based systems generally are adequate to handle water-based adhesives. Increased air flow rates and longer oven bake cycle times are required to evaporate water, however, so process flow can be affected and energy usage may increase.

Hot melt adhesives also have several environmental and energy advantages. As no solvents are used in hot melts, they do not contribute to smog formation. In part because no drying oven is needed, hot melt pressure sensitive adhesives require far less energy to process than most other adhesive types (Maletsky and Villa 1981). The percent solids in the formulation directly influences the amount of energy saved; this percentage varies depending on the application. One drawback of hot melts is that the presence of hot equipment may be a danger to workers (Fullhart and Mottershead 1980).

The advantages of radiation cured adhesives are low energy costs and reduced emission of waste effluents and polluting gases and liquids.

Both moisture cure adhesives and reactive liquids achieve compliance with VOC regulations because they contain no solvents. Moisture cure systems also need no driers, and thus save energy (D'Autilio 1983). The application equipment is more compact than that of solvent-based systems, but moisture cure adhesives cannot use existing solvent application equipment (Morphy et al. 1987). Moisture-cured adhesives and sealants, especially silicones, evolve small amounts of methanol, acetic acid, or other products of the moisture reaction. There is some concern that the catalysts used with reactive liquid systems are, in some cases, hazardous or toxic substances (Dawnkaski 1991).

6.6 POTENTIAL GLOBAL REDUCTION OF 1,1,1-TRICHLOROETHANE USE IN THE ADHESIVES INDUSTRY

There is limited data on the worldwide market for adhesives; however, information is available on the U.S., European, and Japanese markets. The 1983 adhesive demand in the U.S. and Europe was 4,900 million dry formulated pounds and it grew at an annual rate of 3.9 percent to approximately 5,900 million pounds in 1988 (Broxterman 1988). The U.S. portion of this demand is significantly larger than the European portion, representing about 4,600 million pounds, or 75 to 80 percent of the estimated demand in 1988. The Japanese market is considered roughly equivalent to the European market, together consuming 1,300 million dry pounds of adhesives in 1987 (O'Driscoll 1988). Approximately 40-50 thousand tonnes of 1,1,1-trichloroethane was used in adhesives in these countries in 1985 (ICF 1989). Table VI-3 shows the U.S. and European adhesive demand by segment.

As mentioned above, there has been a worldwide trend away from the use of solvent-based adhesives. The cost savings associated with water-borne and hot melt systems are such that this trend would continue even in the absence of the Montreal Protocol's provisions.

6.7 SUITABILITY OF ALTERNATIVES FOR DEVELOPING COUNTRIES AND SMALL QUANTITY USERS

Most established alternatives to 1,1,1-trichloroethane solvent adhesives can be used in developing countries and by small quantity users. Some systems, hot melts for example, require a larger capital investment for equipment, although the cost per application compares favourably. The cost of converting to an alternative adhesive system may be a hurdle in some situations.

Table VI-3. ESTIMATED U.S. AND EUROPEAN ADHESIVE DEMAND BY SEGMENTS -- 1988

Market Segment	Estimated 1988 Demand U.S. and Western Europe Millions of Dry Formulated Pounds	Percent
Packaging	2,500	42.4%
Non-Rigid Bonding	1,100	18,6
Construction	1,000	16.9
Tapes	500	8.5
Rigid Bonding	400	6.8
Transportation	300	5.1
Consumer	100	1.7
TOTAL	5,900	100.0

Source: Based on Broxterman 1985.

CHAPTER 7

COATINGS AND INKS APPLICATIONS

7.1 BACKGROUND

It is estimated that 48 percent of the U.S. coatings market in 1986 was based on solvent-based formulations. This represents solvent use in coatings in 1989 of 1.7 million metric tons, of which only 1.2 percent or 21,800 tonnes (for Europe, North America, and Japan in 1989) (ECSA, HSIA, JAHCS) was 1,1,1-trichloroethane (Chem Systems, 1989). Water-based coatings accounted for 12 percent of the market; high solids, 11.5 percent; two part-systems, 12 percent; emulsions, 10 percent; powder coatings, 6 percent; and ultraviolet light/electron beam (UV/EB) cured coatings, 1.5 percent of the market. In addition, there are solvent-recovery and low-emissions coating application methods, such as dipping, flow, and curtain coating that are alternatives to the use of spray coating.

7.2 CFC-113 AND 1,1,1-TRICHLOROETHANE USE IN COATINGS AND INKS APPLICATIONS

1,1,1-Trichloroethane is used by manufacturers, printers, and users of protective and decorative coatings and inks. CFC-113 use in the production of coatings or inks is negligible. Therefore, this chapter will focus on the use of 1,1,1-trichloroethane in coatings and inks applications. In coatings, 1,1,1-trichloroethane is used alone or combined with other solvents to solubilize the binding substance which is usually composed of resin systems such as alkyd, acrylic, vinyl, polyurethane, silicone, and nitrocellulose resin. In addition to its good solvency, 1,1,1-trichloroethane is also used because of its nonflammability and fast evaporation rate.[1] These properties also make 1,1,1-trichloroethane a suitable thinner for spray coating applications as well as an excellent solvent for ink applications. Inks are used to print items ranging from wallpaper to dog food bags to beverage bottles and cartons. Many of these uses involve the application of coloured ink to a film (or laminate) in the flexible packaging industry.

Although the overall market for coatings and inks in the U.S. showed relatively slow growth in the 1980s (approximately 1 percent according to U.S. Industrial Outlook 1989), the trend in the late 1980s to replace volatile organic compound (VOC) solvents in coatings and inks formulations with 1,1,1-trichloroethane resulted in a significant increase in 1,1,1-trichloroethane demand. However, this growth in usage of 1,1,1-trichloroethane has reversed in recent years because of the addition of 1,1,1-trichloroethane to the list of substances controlled under the Montreal Protocol.

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[1] In the U.S. 1,1,1-trichloroethane is also used frequently because of its non-volatile organic compound (VOC) status.

7.3 ALTERNATIVES FOR REDUCING OR REPLACING CFC-113 AND 1,1,1-TRICHLOROETHANE USE

The use of 1,1,1-trichloroethane in the production of coatings and inks has been reduced in the early 1990s through more extensive use of several of the aforementioned formulations, specifically water-based coatings and inks, high-solids coatings, and powder coatings. Because these alternative formulations function as well as 1,1,1-trichloroethane-based formulations in most applications, the use of these alternative coatings and inks results only in a difference in handling procedures. These differences should manifest themselves predominantly in storage and distribution as many of these alternatives will be more flammable than their 1,1,1-trichloroethane-based counterparts (SNV 1990a).

7.3.1 Water-based Coatings and Inks

Some coatings contain water rather than conventional solvents. They can be applied using a variety of methods, including: dipping, flow coating, conventional air and airless atomizing, air and airless electrostatic spraying, rotating disks and bells, rolling, continuous coating, centrifugal coating, and tumbling. Recent advances in water-based coating technology have improved the dry-time, durability, stability, adhesion, and application of water-based coatings. Primary uses of these coatings include furniture, electronics in automobiles, aluminum siding, hardboard, metal containers, appliances, structured steel, and heavy equipment. In some water-based coatings, standard solvents are added for ease of application, but even these contain much less solvent than conventional coatings and meet VOC limits since the primary solvent is water. A typical formulation blending water with conventional solvents might contain 80 parts water to 20 parts solvent by volume (UNEP 1992).

Water-based inks for flexographic and rotogravure laminates have been successfully developed and have overcome technical hurdles such as substrate wetting, adhesion, colour stability, and productivity. Solvent-based inks have good wetting properties because of the low surface tension of most solvents. However, water has a relatively high surface tension as compared with most solvents and it requires the use of co-solvents to lower the surface tension to enable the wetting of treated surfaces. A mixture that is 80 parts water and 20 parts alcohol and ethyl acetate by volume will achieve an effective surface tension. The ability of the water-based ink to adhere to the film can be enhanced by treating the film by means of accepted methods such as use of primers or heat. About 55 percent of the flexographic inks and 15 percent of the gravure inks used in the U.S. in 1987 were water-based. Continued growth of aqueous inks has been projected by various industry sources.

7.3.2 High-Solid Coatings

Although high-solid coatings resemble conventional solvent coatings in appearance and use, high-solid coatings contain less solvent and a greater percentage of resin. They are applied using methods similar to those used for water-based coatings. High-solid coatings are currently used for appliances, metal furniture, and a variety of construction equipment. The finish of high-solid coatings is often superior to that of solvent-based coatings, despite the fact that high-solid coatings require much less solvent than do solvent-based coatings.

7.3.3 Powder Coatings

Powder coatings contain the resin only in powder form and thus have no solvent. They are applied using fluidized beds, electrostatic spray, and electrostatic fluidized beds. The object to be coated is heated above the powder's melting point, so that when the object is removed from the presence of heat, the resin fuses into a continuous film. The resin then hardens to form a finish that has excellent durability and corrosion resistance. While powder coatings were first used only for electrical transformer covers, they are now used in a large number of applications, including:

- underground pipes;
- electrical components;
- concrete reinforcing bars;
- appliances;
- automobiles;
- farm and lawn equipment;
- lighting fixtures;
- aluminum extrusions;
- steel shelving; and,
- some furniture.

7.3.4 UV/EB-Cured Coatings and Inks

UV/EB-cured coatings and inks have been used in very limited applications over the last 20 years, but their use has seen a dramatic increase in recent years. Several of the markets in which UV/EB-cured coatings and inks have been used more frequently in recent years are flexographic inks and coatings, wood furniture and cabinets, and automotive applications. It is estimated that the usage of UV/EB-cured products has grown by 11 percent annually in North America between the years 1988 and 1993, and this growth is expected to continue for another five years. Annual growth in Europe is estimated at 5-6 percent. Although this growth is expected to slow in the future, UV/EB-curing is likely to remain popular in niche applications (MPC 1994b). One business manager for a supplier of these coatings has estimated that UV/EB coatings' share of the worldwide paint and coatings market will double over the next 5 to 7 years (MPC 1994a).

There are several factors which contribute to the growing popularity of UV/EB-cured coatings and inks. These include: high quality, rapid cure times, low energy use, small space requirements, elimination of some handling problems, and reduction in emissions of ozone-depleting substances and VOCs. One major limitation to the use of UV/EB-cured coatings and inks is outdoor durability (MPC 1994b). This is an especially important consideration in automotive applications.

7.4 ENVIRONMENTAL AND ENERGY CONSIDERATIONS

Goods are printed or coated with solvent-based coatings and inks in a continuous process. Once the coating or ink has been applied, the product passes through a drying step where the solvent is emitted through evaporation.

Solvent recovery systems such as carbon adsorption can be used to capture these solvent emissions. As discussed earlier, technological innovation is overcoming the stabilization problems which sometimes occur.

The types of coatings and inks described in this chapter as alternatives to formulations containing 1,1,1-trichloroethane reduce solvent emissions by reducing or eliminating the use of conventional solvents. Therefore, the environmental impacts associated with such solvent emissions are also reduced.

CHAPTER 8

AEROSOLS APPLICATIONS

8.1 BACKGROUND

Aerosol packaging is a popular method for storing and dispensing consumer and industrial products ranging from insecticides to hair sprays. In 1986, the worldwide aerosol industry produced an estimated 6.8 billion units. Western Europe was the largest producer, followed by the United States and Asia. 1,1,1-Trichloroethane consumption in aerosol applications in the U.S. was approximately 18,590 metric tonnes (ICF 1989a). It is estimated that Western Europe and Japan consumed 12,425 and 10,790 metric tonnes of 1,1,1-trichloroethane in 1984, respectively (ICF 1989a). The Aerosol Industry of Japan estimates that consumption of 1,1,1-trichloroethane in the Japanese aerosol industry had dropped to 5,000 metric tonnes in 1990 (Kurita 1991b). No data are available for the rest of the world. No information is currently available on current chlorinated solvent consumption trends in Western Europe, Japan, and the rest of the world, therefore, the discussion that follows focuses on the U.S. market for aerosols. The major aerosol product end-uses where 1,1,1-trichloroethane is used includes automotive and industrial products, pesticides, and household products (ICF 1989a).

8.2 CFC-113 AND 1,1,1-TRICHLOROETHANE USE IN AEROSOL PRODUCT APPLICATIONS

In an aerosol package, the contents are stored under pressure in a metal container and dispensed in a controlled manner by activating a valve. The continued effect of the type of propellent used, the shape of the opening from which the contents are expelled from the can, and the composition of the product determine the form in which the product is delivered. This form can range from a fine mist (the most common) to a liquid stream to a foamy lather. In general, the components of an aerosol are the active ingredient, the solvent or carrier, and the propellant. The active ingredient is responsible for the effectiveness of the product (i.e., the ingredient that allows a cleaner to clean); the solvent or carrier solubilizes all ingredients in the formulation to allow for uniform dispensing of the product; and the propellant expels the contents from the can.

1,1,1-Trichloroethane functions as either an active ingredient (e.g., degreaser or cleaner) or as a solvent in aerosol product formulations. 1,1,1-Trichloroethane's high density adds to container weight while its high stability translates to a long shelf life. Other properties that make 1,1,1-trichloroethane especially well-suited for aerosol applications are its nonflammability, excellent solvent properties, high evaporation rate, and ability to generate a spray of small particle size. Quick evaporation allows 1,1,1-trichloroethane to deliver the active ingredient efficiently and a small particle size results in a good spray pattern.

Though most of the aerosol applications traditionally used 1,1,1-trichloroethane as their solvent, there are a small number of products which made use of CFC-113 as well. Probably a few tens of tonnes per year of CFC-113 were used annually in the late 1980s. The application where CFC-113 was most often used as a solvent is in the removal of flux from electronic components such as printed circuit boards (PCBs). In these products, CFC-113 was often mixed with another chemical such as isopropyl or ethyl alcohol. These product mixtures were often used due to the fact that they act as both degreasers and cleaners, and leave very little residue on evaporation.

Conformal coatings also make use of CFC-113. These products are sprayed on printed circuit boards and other electronic components to serve as a sealant. Over a wide range of temperatures, these coatings protect equipment from environmental conditions which would normally damage the equipment. Depending on the resin used in the coating, 1,1,1-trichloroethane is sometimes included as well.

Finally, CFC-113 is often used in aerosol application for contact cleaners. The cleaners are used as part of the routine maintenance of electrical equipment in order to prevent malfunctions which might occur from everyday pollutants. Because this equipment is often cleaned while energized, it is important that the aerosol cleaner be nonflammable, thus making CFC-113 an attractive ingredient. Use of these cleaners helps to maintain continuity within electrical circuits (Chemtronics 1989).

8.3 ALTERNATIVES FOR REDUCING OR REPLACING CFC-113 AND 1,1,1-TRICHLOROETHANE USE IN AEROSOL PRODUCTS

Most aerosol products currently employing CFC-113 and 1,1,1-trichloroethane can be reformulated with alternative compounds. Table VIII-1 lists substitute solvents and the major product application areas. From a number of properties determining product performance, two performance factors are considered of most importance: flammability and density. These factors are also listed across the top of the table. Except for water, some hydrochlorofluorocarbons (HCFCs), and non-ozone-depleting chlorinated solvents (e.g., trichloroethylene, perchloroethylene, methylene chloride), all of the substitute solvents currently available are more flammable than 1,1,1-trichloroethane. The flammability is also a function of the propellant; butane and propane being more flammable than carbon dioxide, nitrous oxide or the traditional CFC-11/CFC-12 mixture.

Alternative solvents currently exist for virtually all aerosol solvent applications of CFC-113 and 1,1,1-trichloroethane. However, while some of these alternatives are functional, they are considered to be less than optimal for a variety of reasons. For example, in applications where a strong solvent is required, but the use of a flammable solvent would pose serious safety risks, substitutes may include only hydrofluorocarbons (HFCs), HCFCs and chlorinated solvents. While these solvents would be functional, HCFCs contribute to ozone-depletion, and chlorinated solvents are toxic and may pose health risks to workers and users of a product.

Table VIII-1. SUMMARY OF SUBSTITUTE SOLVENTS FOR 1,1,1-TRICHLOROETHANE AND CFC-113 IN AEROSOLS

	Major Product Applications			Performance Factors	
	A&I	Pest	HH	Flammability	Density
1,1,1-Trichloroethane	*	*	*	None	1.32
CFC-113	*			None	1.57
Substitute Solvents:					
Petroleum Distillates	*	*	*	High	0.75
Aromatic Hydrocarbons	*		*	High	0.87
Alcohols	*	*		High	0.80
Ketones	*		*	High	0.81
Water Systems	*	*	*	Low to None	1.00
Dimethyl Ether		*		High	0.66
Chlorinated Solvents	*	*	*	None	1.31-1.62
HCFCs	*	*	*	None	1-1.21

* Denotes that the substitute solvent can be used in the product application indicated.

A&I	:	Automotive and Industrial Products.
Pest	:	Pesticides.
HH	:	Household Products.

Source: Based on ICF 1989a.

8.3.1 Reformulation Using Petroleum Distillates

One alternative for the replacement of CFC-113 and 1,1,1-trichloroethane in aerosol products is reformulation using petroleum distillates. Due to the high flammability of the petroleum products, reformulation from CFC-113 and 1,1,1-trichloroethane to petroleum distillates can only be performed in select applications and with proper explosion proof equipment. Commercially available products reformulated with petroleum distillates and other hydrocarbon solvents exist for various automotive products such as tire cleaners, lubricants, spray undercoatings, and in household products such as water repellents/shoe waterproofers, glass frostings, and insecticides. Extreme care must be exercised in both the manufacture and use of these products to reduce the risk of explosion.

8.3.2 Reformulation to Water-based Systems

Reformulation from 1,1,1-trichloroethane or CFC-113 to water-based systems can be performed in a number of applications, including shoe polishes, foggers (partial or total release insecticides used to control infested rooms), mould release agents, and fabric protectants. The major disadvantage/concern of reformulation of 1,1,1-trichloroethane or CFC-113 to water-based systems is the effectiveness of the final product. These concerns arise from several fundamental differences in the systems. For example, it is generally agreed that water-based foggers are less effective because they do not disperse well and they result in large particle sizes (Ortho 1989, McLaughlin Gormley King Company 1989, Sprayon 1989). These factors make the foggers less effective than foggers which utilize 1,1,1-trichloroethane since the water tends to be ineffective at penetrating the exoskeleton of insects. Tests are currently underway to produce water-based solvent mixtures which will be able to overcome this problem.

Other drawbacks associated with water-based aerosol products include long drying time and inability to sufficiently wet the surface being sprayed. The relatively slow evaporation rate of water as compared to that of CFC-113 or 1,1,1-trichloroethane results in a slow drying time. While the drying time can be accelerated with the application of heat, it is still likely to be significantly longer than the drying times associated with CFC-113 and 1,1,1-trichloroethane. Also of concern in some applications is the reduced wettability of a formulation that has been reformulated to use water as the primary solvent. The high surface tension of water often results in less efficient wetting of surfaces being sprayed. This is an especially important consideration in applications such as mould release agents (UNEP 1994b).

Despite these drawbacks, water-based aerosol formulations are becoming more common in a wide variety of industries, especially among those wanting to avoid the use of flammable solvents, HCFCs, and chlorinated solvents.

8.3.3 Reformulation Using Organic Solvents

There are a number of alternative organic solvents that can be used to replace CFC-113 or 1,1,1-trichloroethane in many aerosol applications. These alternative solvents include petroleum distillates, alcohols, ketones, and terpenes. These solvents are capable of removing a wide variety of contaminants, and all are currently used in commercially available aerosol products. This strong cleaning power, coupled with the ability to solubilize other active ingredients, makes these alternative solvents attractive substitutes for CFC-113 and 1,1,1-trichloroethane.

There are two primary drawbacks associated with the reformulation of aerosol products using organic solvents -- flammability and environmental impact. All of the aforementioned organic solvents are flammable and must therefore be used with extreme caution to reduce the risk of explosion and fire. While many users are able to safely implement flammable formulations with only minor process and handling changes, others may not be able to overcome the risks associated with the flammability of the solvents. For example, flammable solvents are not a viable alternative for the in-situ cleaning of energized equipment. The major environmental concern associated with these organic solvents is their impact on the formation of smog and other ground-level pollution. In the United States, virtually all of these solvents are classification as volatile organic compounds (VOCs) and their use is severely restricted in some geographic areas. Nonetheless, where flammable solvents are acceptable, reformulation using organic solvents is an attractive option.

8.3.4 Reformulation Using Nonozone-Depleting Chlorinated Solvents

Reformulating aerosol products to use nonozone-depleting chlorinated solvents in place of CFC-113 or 1,1,1-trichloroethane is an option in limited applications. The chlorinated solvents that might be used are trichloroethylene, perchloroethylene, and methylene chloride. The primary benefit associated with these alternatives is their nonflammability. This property makes them one of the few viable alternatives for aerosol cleaners used on energized equipment.

Potential formulators and users of aerosols containing these solvents must be aware of their associated human health risks. All three of these alternatives are potentially carcinogenic to humans and have accordingly low occupational exposure limits (UNEP 1994a).

8.3.5 Reformulation Without a Solvent

In some cases where CFC-113 or 1,1,1-trichloroethane is used only as a solvent or carrier, and not as an active ingredient, it may be possible to reformulate the aerosol product to function without the use of a solvent. In these nonsolvent systems, the active ingredient of the product is dispersed solely by the force of the propellant. Such a formulation is currently being marketed by several manufacturers of aerosol mould release agents, who have observed increased performance in some applications because there is no longer any possibility of the solvent attacking plastics or metals with which it comes into contact. However, it is also possible to obtain inferior performance, primarily because of the uneven dispersion of the active ingredient which may occur in the absence of a solvent carrier (UNEP 1994b).

8.3.6 Reformulation Using HCFCs

Another alternative for replacing CFC-113 and 1,1,1-trichloroethane in limited aerosol applications is reformulation with HCFCs. At the present time, HCFC-141b is the only commercially available alternative, although it is expected that HCFC-225 will become available for aerosol applications in the near future. HCFC solvents have much the same properties as CFC-113 and

1,1,1-trichloroethane, making them ideal replacements from a technical standpoint. However, HCFCs are ozone-depleting substances and will therefore add further to depletion of the ozone layer. HCFC-141b has an ozone-depletion potential (ODP) comparable to that of 1,1,1-trichloroethane, and should therefore not be used as a substitute for 1,1,1-trichloroethane. It is important to note that HCFCs are a transitional substitute at best because they are scheduled for a complete phaseout under the Montreal Protocol by the year 2030. In addition, certain countries have restricted the use of HCFCs in some applications. Given these considerations, HCFCs should only be considered in applications where a nonflammable formulation must be used, and even then, when no other alternative is satisfactory.

8.3.7 Alternative Delivery Systems

CFC-113 and 1,1,1-trichloroethane use in aerosols can also be reduced if alternative means of delivering the product are developed. Two examples of these alternative methods are: (1) a manual "wet-brush" (recirculating liquid) system, as a substitute for aerosol brake cleaners used in repair shops, and (2) increased use of professional dry cleaning services as a substitute for the use of aerosol spot removers. Although more examples of alternative non-aerosol methods can be found for the other aerosol products that currently use CFC-113 and 1,1,1-trichloroethane, the cost data presented in this chapter uses these two applications as examples.

8.4 COSTS OF ALTERNATIVES

Table VIII-2 presents the costs for the two groups of control technologies for reducing 1,1,1-trichloroethane use in aerosol products: (1) the reformulation of aerosol products, and (2) a switch to an alternative method to deliver the product other than by means of an aerosol. The methodology used to estimate the costs associated with the reformulation of aerosol products currently using 1,1,1-trichloroethane is based on a previous analysis (ICF 1989b) and includes the estimation of reformulation costs per plant (i.e., R&D, marketing, and capital costs), the number of aerosol plants that would incur these costs (based on the production volume of an average "model" plant), and the calculation of total annualized cost.

Using reformulation with petroleum distillates as an example, it is easy to see the effects of such a change on the production cost of aerosol products. Looking first at the cost of the product itself, the use of this new solvent will most likely increase the cost of the container in which it is distributed. Due to the fact that the petroleum-based solvents have a density of about 0.75, as compared to 1.32 for 1,1,1-trichloroethane, a larger container will be needed in order to hold a similar weight of the product. This is a significant consideration since the cost of the packaging accounts for almost 36 percent of the product cost to the manufacturer (ICF 1989).

For the case of petroleum distillates, the change from 1,1,1-trichloroethane use will necessitate expenditures in research and development, labelling, and public education. Due to the flammable nature the new solvent, a public education program might be needed to inform potential users of the proper precautions which should be taken when using the product. In addition, increased research and development will be needed to search for ways by which

TABLE VIII-2. COSTS OF CONTROLS FOR 1,1,1-TRICHLOROETHANE IN AEROSOLS

Control Option	Incremental Costs[a] (thousand dollars) Capital	R&D and Marketing[b]	Total Annualized Costs[c]
Reformulation to:			
Petroleum Distillate	--	5,594	622.7
Water-based Systems	92.3	2,244	260.2
Alternate Delivery Systems			
Occupational Uses	170,700[d]	--	19,000.0
Consumer Uses	--	--	--

[a] Raw material costs are not considered in this analysis primarily because the replacement chemicals in both, the reformulated products and the alternate delivery systems are as expensive as 1,1,1-trichloroethane.

[b] Includes R&D and marketing costs associated with the reformulation of various automotive and industrial products, household products, and aerosol pesticides currently using methyl chloroform.

[c] Costs are discounted at the social rate of discount (2 percent) over the equipment lifetime (10 years).

[d] These costs represent the capital investment required if all users of 1,1,1-trichloroethane-based brake cleaners purchased alternative equipment.

the reformulated solvent might be made safer and more efficient. Finally, retrofitting of assembly line equipment will most likely be needed in order to provide adequate measures for fire-prevention as well as firefighting (ICF 1989a).

The example just presented is perhaps the most extreme case. Though the cost impacts of other alternative solvents may not be as extensive as those for petroleum distillates, they may be significant.

The costs of the two options considered in the alternative delivery system category include the costs incurred by the current users of aerosol products (e.g., brake shop owners and consumers) and do not include costs to the aerosol industry. It is estimated that aerosol manufacturing facilities could either reformulate these products or produce other aerosol products without incurring major financial losses.

An example of an alternative to consumer use of 1,1,1-trichloroethane-based spot-removing aerosols is the use of professional cleaning services. Aerosol spot removers are designed to reduce consumers' dry-cleaning costs by providing consumers an easy way to remove spots from dry-cleanable garments. Most of the industry for aerosol spot removers has reformulated products to use HCFCs in place of 1,1,1-trichloroethane. In the event that aerosol spot removers were no longer available, consumers would be forced to resort to additional dry cleaning services. These costs are based on the increase in the number of times that consumers will have dry cleaners remove spots from garments that the consumer could have treated him or herself with aerosol spot removers (ICF 1989b).

The data used in this analysis includes experimental data on the number of spot treatments obtainable from a can of aerosol spot removers, the likely interval between dry cleaning events, the size of the spot remover market, and current dry cleaning fees. Spot removers used 1.1 million kilograms of 1,1,1-trichloroethane in 1987. The results of this analysis indicate that additional dry cleaning costs to consumers are approximately $20 per kilogram of 1,1,1-trichloroethane used. These are upperbound costs, because a portion of current users of aerosol spot removers might decide to "live with the spot" a little longer, taking the garment to a dry cleaning service only when it became time for general cleaning of the garment. In this case, additional dry cleaning expense would be avoided. Even in this case, however, costs would probably be higher, compared to other 1,1,1-trichloroethane controls, since consumers pay more to have a spot treated by a professional dry cleaning service than they do if they use aerosol spot removers.

Aerosol brake cleaners are used by brake mechanics to (1) remove oil, grease and brake fluid from the brake drum system, (2) remove the excess dust accumulated inside the brake housings, and (3) remove glaze from brake pad surfaces. To remove oil, grease, and brake fluid, the best alternative to an aerosol is to degrease manually, using a petroleum-naphtha-based solvent and an ordinary scrub brush. To remove excess dust and glaze, there are several alternatives to cleaner application by aerosol, including vacuum enclosures, recirculating liquid systems, and wet brush systems. The liquid applied generally contains water and a surfactant (PEI 1983). The wet-brush is the lowest-cost option. It is estimated that there are 297,416 brake repair shops that employ aerosol brake cleaners (PEI 1983). The cost of substituting with the wet-brush system is $574 per shop, so the investment for all shops would amount to $170.7 million. Operating costs are assumed to be approximately the same as the current costs of aerosol brake cleaners; thus, the cost of the equipment is believed to be indicative of the additional costs incurred. Using 10-year and 2 percent discount rates, annual costs amount to approximately $19 million.

CHAPTER 9

OTHER SOLVENT USES OF OZONE DEPLETING SUBSTANCES (CFC-113, 1,1,1-TRICHLOROETHANE AND CARBON TETRACHLORIDE)

9.1 BACKGROUND

Some amount, in most cases relatively small quantities, of CFC-113, 1,1,1-trichloroethane, and carbon tetrachloride are employed in a number of industry and laboratory applications. These include:

- bearer media for coating and impregnation
- vapour soldering technology
- component drying
- riveting and machining
- airplane hydraulic system testing
- fabric protection and coating
- semiconductor manufacturing
- miscellaneous testing (including leak detection)
- mould release agents
- film cleaning
- component cooling
- manufacture of solid rocket motors
- oxygen systems cleaning
- correction fluids
- fabric spot remover
- process solvents

The Committee consensus is that by 1996, in accordance with the Montreal Protocol, most of the CFC-113, 1,1,1-trichloroethane, and carbon tetrachloride used for these applications could be replaced by the alternatives discussed in this chapter.

In the applications of laboratory analyses and in the manufacture of a specific large scale solid rocket motor, the Parties have granted an exemption for continued use of specified ozone-depleting solvents for 1996 and 1997. The exemptions are subject to review and alternatives are being investigated.

In the case of use of ozone-depleting substances as process chemicals, there are also a number of alternatives identified in this report. In addition, an in-depth review of alternatives is planned for completion and presentation by the Technical and Economic Assessment Panel to the Parties by early 1995.

9.2 BEARER MEDIA FOR COATING AND IMPREGNATION

In some applications, CFC-113 is used as a carrier of lubricants that reduce frictional damage. In a typical process, gold-plated contacts are dipped into a bath of CFC-113 containing two percent of a lubricant such as perfluorinated polyether. The CFC-113 acts both as a cleaner and a lubricant bearer. The following alternatives have been identified for this application (Nordin 1988, Owens 1990):

- Use of mechanical methods, such as spraying or rolling, to dispense the lubricant. (The problem of excessive application of the lubricant must be solved as the lubricant must not exceed four micrograms per contact.
- Application of the lubricant via emulsions. (These should be water-based emulsions if possible.)
- Use of an alternative non-halogenated solvent compatible with fluorinated lubricants.
- Use of an alternative lubricant. (The lubricants should be compatible with the materials in use.)
- Use of a perfluorinated solvent has been demonstrated with perfluoropolyether lubricants and is in commercial use in several countries. However, because of the high global warming potential of perfluorinated solvents, they should only be used in applications where emissions can be kept at or near zero.
- Hydrochlorofluorocarbons (HCFCs) might be considered despite their small contributions to ozone-depletion. It is important that HCFCs only be used where other alternatives are considered unacceptable, and that recovery systems be used in conjunction with HCFCs.
- HFCs might be considered despite their contributions to global-warming. It is important that HFCs only be used where other alternatives are considered unacceptable, and that recovery systems be used in conjunction with HFCs.

9.3 VAPOUR SOLDERING TECHNOLOGY

Vapour-phase soldering, also known as condensation soldering, is a reflow method that involves boiling a liquid and putting the cool electronic assembly along with unmelted solder into the hot vapour. The vapour raises the temperature of the cool electronic assembly and the solder until the solder melts. Because of its all-around heat application, vapour-phase soldering is one of a limited number of soldering processes that, in principle, enables both sides of a substrate to be soldered simultaneously. It cannot, however, be used as the only soldering process in mixed assemblies because the process can damage temperature-sensitive bodies on some leaded components (Pawling 1987).

The primary liquids used in vapour-phase soldering -- nonflammable perfluorinated organic compounds -- are nonozone-depleting but costly. In addition, they have a very high global warming potential. To minimise primary vapour losses, a less expensive secondary vapour blanket using a chemical with a lower boiling point, such as CFC-113 (boiling point 47.6°C), is often used.

With standard top loading batch equipment, this cuts losses of the primary vapour by a factor of ten (Seidinger 1989). CFC-113 also serves as a conduit for the release of toxic hydrofluoric acid and perfluoroisobutylene (PFIB) that may be generated if the primary vapour overheats. To minimise vapour losses and reduce emissions of toxic compounds, the blanket should be operated at a low temperature. The interface of the two vapours forms a zone where the secondary vapour can also break down, releasing hydrochloric and hydrofluoric acids, phosgene, and carbonyl fluoride. Treating the condensate will not only eliminate most of these dangerous by-products but will also reduce corrosion of the machine itself.

Two possible alternatives to using CFC-113 to form a secondary vapour blanket in reflow soldering include:

- Eliminating the use of a secondary vapour blanket. Although joint quality would not suffer, eliminating the secondary blanket could increase production costs for the reflow soldering operation by a factor of 10. A primary vapour recovery unit that claims to recover up to 80 percent of any primary vapour entering the extraction system is now available. With this unit, net fluid costs could be reduced from approximately U.S. $10-14/hour to U.S. $3-4/hour.

- Using a secondary vapour blanket that does not deplete the ozone layer. Recently a perfluorocarbon liquid has been introduced as a possible substitute for the secondary blanket. The compound has a half life of approximately 1,000 years and does not contain chlorine, bromine, or hydrogen atoms. (Niemi 1991) However, the extremely long atmospheric lifetime of perfluorocarbons give them high global-warming potentials. Therefore, they should only be used in equipment that is specially designed to minimise emissions. To replace perfluorocarbons in this and other applications, an alternative known as hydrofluorocarbons (HFCs) are currently being developed.

Where specifications and throughput allow, IR soldering is also an alternative process. Table IX-1 summarises a recent evaluation comparing the use of CFC-113 and a perfluorocarbon as the secondary blanket in vapour-phase soldering equipment. The results of this test show:

- CFC-113 and the perfluorocarbon are consumed in similar quantities.

- The rate of corrosion is somewhat lower for the perfluorocarbon, as measured by the copper wire method.

- An equivalent amount of PFIB is generated for both chemicals.

- The amount of total hydrohalic acids generated is much lower for the perfluorocarbon.

Table IX-1. COMPARISON OF CFC-113 AND A SUBSTITUTE PERFLUOROCARBON AS A SECONDARY VAPOUR BLANKET

Characteristic	CFC-113	Perfluorocarbon
Rate of Consumption (m^3/hr)	1.14-1.51 x 10^{-4}	1.14-1.51 x 10^{-4}
Vapour Temperature (°C)		
Secondary vapour	55-60	58-61
Primary vapour	216-218	217-218
Rate of Corrosion (mm/yr)	5.59 x 10^{-2}	2.03 x 10^{-2}
Perfluoroisobutylene Generation (μgm/m^3/hr)	<0.227	<0.227
Hydrofluoric Acid Generation (μgm/m^3/hr)		
150°C	682 (8 HCl)	1140
215°C	9,090 (240 HCl)	4420

Source: Seidinger 1989

9.4 COMPONENT DRYING

Many precision devices, such as electrical and electronic parts, mechanical assemblies, optical equipment, and delicate instruments, come into contact with water during manufacturing and assembly. Such parts must be dried promptly after cleaning to prevent rusting, water staining, and general deterioration in quality that can lower product reliability. A dedicated drying or dewatering process is often used to remove moisture. Typical techniques include:

- centrifugal processing followed by hot air drying
- absorbent drying using alcohols, such as ethanol, isopropanol, and acetone
- vapour drying with non-CFC solvents, such as chlorocarbon
- displacement or solubilisation drying using CFC-113-based drying formulations (Johnson 1991).

The trade-offs among these drying techniques are compared in Table IX-2.

Process recovery and conservation methods for CFC-113 in drying are similar to those in typical solvent cleaning systems. The use of CFC-113 for drying represents, perhaps, less than 10 percent of the CFC-113 used for cleaning, but many of the applications are critical (Johnson 1991).

9.4.1 Semiconductors[1]

Integrated circuits, the major product of the semiconductor industry, are a combination of electronic devices including transistors, diodes, resistors, and capacitors which are placed in a single semiconductor crystal. During the fabrication of integrated circuits, CFC-113 is used for displacement drying of semiconductor materials, such as wafers. Depending on the integrated circuit being made (e.g., metal oxide semiconductors (MOS) or bipolar), different process steps, which can include wafer preparation, oxidation, doping, and layering, are repeated so that drying may occur many times during the fabrication process.

9.4.2 Printed Circuit Boards

Of the four processes commonly used for critical drying of printed circuit boards during manufacturing, two processes use CFC-113. These processes involve:

- Dipping the wet boards in a circulating bath of pure CFC-113. The water is displaced, floats on the solvent surface, and is pumped off the surface into a separator so that the boards are not re-wetted when removed. Following this bath, the board is usually passed through a vapour degreaser containing a CFC-113/ethanol azeotrope to remove residual water traces.

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[1] Semiconductors are materials having an electrical conductivity between that of a conductor and an insulator. They are either discrete devices such as transistors or thyristors, or integrated circuits that contain two or more devices in a single semiconductor crystal.

Table IX-2. COMPARISON OF DRYING TECHNIQUES

Dewatering Technique	Advantages	Disadvantages
Centrifugal processing and hot air drying	Low equipment cost, handling.	Can be used for simple shape products. High energy costs, spots.
Absorbent drying using alcohols	Drying at room temperature.	Large solvent consumption. Needs fire protection measures.
Displacement drying with PFCs and HCFCs	Satisfactory drying at 50°C or below.	High cost of solvents. Bear in mind ODP and GWP.
Displacement drying with chlorinated solvents	Proven, available, possible to retrofit equipment	Possible compatibility with materials. Requires careful management and handling.
Displacement drying using CFC-113	Energy efficient, rapid drying.	Higher equipment costs. Increasing operating costs. May leave a residual film. Depletes stratospheric ozone layer.

Source: Johnson 1991.

- Dipping the wet boards into a surfactant/CFC-113 mixture to emulsify the water, then using a vapour degreaser to remove the surfactant.

The other two critical drying processes use alternative solvents. The circuits can be dried by:

- Dipping the wet boards into two successive isopropanol tanks fitted with dryers

- Dipping the wet boards into a water-displacement product based on toluol. The water drains through a grid in the bottom of the tank.

CFC-113 use could be eliminated by switching to these two alternative drying processes.

Another method for eliminating CFC-113 in this application is to eliminate the use of water in the manufacturing process, thereby eliminating the need for drying. Alternatives to the use of water-based processes are discussed in detail in the chapter on Electronics Cleaning. For manufacturers using small quantities or operating in developing countries, alcohols and alcohol/perfluorocarbon mixtures are suitable alternatives to CFC-113 and 1,1,1-trichloroethane, for unlike aqueous and semi-aqueous processes, water treatment systems are not required (Matsui 1991).

9.4.3 Mechanical Assemblies

For further information, refer to the chapter on Precision Cleaning.

9.4.4 Metal Surfaces

For further information, refer to the chapter on Precision Cleaning.

9.5 RIVETING AND MACHINING

CFC-113 is used as a lubricant and coolant in certain drilling and riveting operations during the manufacture of aircraft frames, particularly wing assemblies. In this operation, an automatic drill/riveting machine clamps the aircraft skin and stringer together, drills and countersinks a close tolerance hole through the two pieces, inserts and compresses a rivet, and shaves the rivet flush to provide an aerodynamically smooth surface. The entire operation takes approximately seven seconds. CFC-113 is used primarily to carry away heat generated during the drilling and shaving processes, which extends the bit life of the drill and improves the finish of the hole. For one company, CFC-113 also lubricates the rivet as it is inserted and prevents corrosion in the riveted area after assembly. For some applications, lubrication of the rivet is critical to ensure that the rivet completely expands into the drilled hole. Incomplete "fill" leads to fatigue stress and the possibility of leakage from fuel tanks located in the wings of the aircraft.

Manufacturers agree that non-evaporative lubricants are adequate for holes less than two or three hole diameters in depth. For deeper holes, lubricants combined with cold air is considered more promising. Possible substitutes for CFC-113 in shallow holes include long chain fatty alcohols and emulsified water/oil mixtures. Manufacturers agree that the ideal substitute must:

- have appropriate coolant/lubricity characteristics
- be nontoxic and nonflammable for worker safety
- leave no residue that could prevent good bonding of paints and sealants
- be noncorrosive

Additional research is needed to determine whether non-CFC alternatives will meet these requirements. In recent years, the International Cooperative for Ozone Layer Protection (ICOLP) has promoted intercompany research between McDonnell-Douglas, Boeing, and British Aerospace on alternative methods of riveting (British Aerospace 1990; Grumman Aircraft 1990).

9.6 AIRPLANE HYDRAULIC SYSTEM TESTING

New airplane hydraulic systems are routinely tested for leaks by adding hydraulic fluid through existing airplane ground service connections, pressurizing a portion of the system, and then visually inspecting for leaks. Discovered leaks are stopped and spilled hydraulic fluid is cleaned up. This process is repeated at higher pressures for each portion until the entire hydraulic system is pressurized to 3000 psi (210 kg/cm^2) without leaks. CFC-113 is used to clean up the spilled hydraulic fluid. This solvent is necessary because it can be used inside the airplane fuselage without flammability or toxicity problems. Also, because CFC-113 is more dense than hydraulic fluid and completely evaporates, it is possible to flush inaccessible areas without concern for corrosion.

A new process that significantly reduces the use of CFC-113 has recently been used for hydraulic systems testing. The process uses inert gas and audio inspection. Pressurized nitrogen is introduced into the hydraulic system through a hydraulic pump filter module. As the gas enters the system, it bypasses component valves that are designed to operate under hydraulic fluid pressure. Bypassing these valves allows the entire system to be filled at once, including the fluid reservoir which has a 75 psi (5.3 km/cm^2) relief valve. Although this relief valve limits the maximum pressure that can be applied to the system, it is still great enough to force gas through system leaks that would require much higher pressure if hydraulic fluid were used. By using an ultrasonic sound detector tuned to the frequency of the escaping gas, a 95% or better leak detection rate is achievable. The new process is very capable of finding major leaks that previously required large quantities of CFC-113 for clean up after testing with hydraulic fluid. The few leaks that show up when the system is finally fully charged with hydraulic fluid are relatively small and require much smaller quantities of CFC-113 for clean up. However, an alternative is still being sought for this reduced, but necessary solvent use.

The new gas leak detection system has reduced CFC-113 consumption for hydraulic spill clean up, on average from 25 to 3 gallons (95 to 11 litres) per plane (Boeing 1991).

9.7 FABRIC PROTECTION AND COATING

1,1,1-Trichloroethane is used as a solvent in fabric protection agents sold for both industrial and consumer use. Like other chlorinated solvents, 1,1,1-trichloroethane "dissolves" the polymeric fluorinated compounds that protect the fabric (teflon, for example), causing them to swell so that a more homogeneous mixture or dispersion can be applied.

There are three general classifications of fabric protection products which use 1,1,1-trichloroethane. The most common is the aerosol can which is widely used by consumers to treat fabrics in their home. The second is for Retailer Applied Fabric Treatment (RAFT), where a retailer provides the application of a fabric treatment, usually for soil or stain protection, as an after sale service. The third application method is mill application. Mill application has a long history and is either done at the mill, where the fabric is manufactured, or by a special contractor who performs the application either for the manufacturer or for a user of the fabric (Mertens 1991a).

The aerosol application is perhaps the largest and most diversified segment as there are many formulators and packagers of aerosol fabric protection products. They are usually based on a fluorocarbon or a silicone resin and use a solvent carrier. The solvent most commonly used is 1,1,1-trichloroethane, primarily due to its excellent solvency, fast evaporation rate, low flammability, low toxicity, and nonphotochemical reactivity (Mertens 1991a).

The Retailer Applied Fabric Treatment is usually found in the retail furniture business and in automotive dealerships. The seller of a piece of upholstered furniture or a fabric automobile interior often offers the application of soil and stain preventative spray after the sale of the product itself. This application uses predominately fluorocarbon resin with some silicone. The fluorocarbon resins are often formulated with 1,1,1-trichloroethane. There is a wide variation in the quality of the application methods in this area. Some of the retailers have large warehouse operations where they can install ventilation booths and have well trained operators performing the application. Others are small operations and may spray on the fabric protection at the loading dock door. Because of these varied application procedures, the properties of 1,1,1-trichloroethane are well suited to this application (Mertens 1991a).

There is also an extension of the RAFT application where fabric protectants are applied in the home. In this application, a service company comes to the consumer's home and applies fabric protection to furniture, drapes, and/or carpeting. The toxicity, flammability, and odour are major factors in the choice of solvents used in these applications. The consumer does not want any lingering odours in the home after the application of the fabric protector, and the applicator needs to be concerned about the flammability and toxicity of the product during the application (Mertens 1991a).

Mill application of fabric protectors is usually performed on an automatic processing machine custom designed for the operation. The advantages of mill application are the ability to cover the cloth completely with the fabric protector and to automate the process. These systems usually incorporate some form of vapour recovery, and because of this, 1,1,1-trichloroethane has not been the solvent of choice for the larger mill treatment operations. Trichloroethylene has often been used where vapour recovery is incorporated into the process (Mertens 1991a).

Replacement of 1,1,1-trichloroethane in fabric protection applications will vary significantly in each of these applications. For example, 3M has developed a hydrocarbon solvent version of its Scotchguard™ fabric protection products. This product is flammable and contains volatile organic compounds (VOCs), and therefore may contribute to the formation of tropospheric ozone (smog). In many areas there are stringent regulations controlling the use of VOCs in aerosol cans, and the use of these alternatives may be restricted in those areas that have high tropospheric ozone levels. In addition, there will be a need for consumer education to illustrate the risks associated with the flammability of such replacement products (Mertens 1991a).

Replacement in RAFT applications will be difficult for those areas that have tropospheric ozone problems. The most likely replacement solvent for this application will be mineral spirits or hydrocarbon solvents. With both types of solvents, the dry time will be extended and the flammability may be of concern to users. Additional capital expense may be required to handle and use these solvents safely (Mertens 1991a).

DuPont has just introduced a water-based fluorocarbon resin system which will replace solvent-based fluorocarbon products that are currently used in this application. The system will require the purchase of special equipment for the application of the water-based product.

Mill applications appear to have the greatest opportunity to change to alternative systems as they can substitute solvents and use add-on controls to minimize emissions of solvents that are VOCs, Hazardous Air Pollutants, toxic, or otherwise pose a threat. Trichloroethylene with carbon adsorption has been successfully used in this application for many years, and can easily be extended to replace any use of 1,1,1-trichloroethane (Mertens 1991a).

Although it is possible to obtain solutions or dispersions of polymeric fluorinated compounds using other solvents such as hydrocarbons and esters, there is still some loss of the solvent effect. In addition to its "swelling" capacity, 1,1,1-trichloroethane also possesses an unusually high density (nearly twice that of other solvents) -- a characteristic which reduces the tendency of the solids to settle. Alternative formulations will require more frequent and thorough agitation to keep the solids suspended.

9.8 SEMICONDUCTOR MANUFACTURING

9.8.1 Plasma Etch Processing

As shown in Table IX-3 (Mocella 1991), several CFC and fluorocarbon compounds are used in plasma etching of silicon wafers. Of these materials, FC-14 (CF_4), CHF_3 and C_2F_6 do not contain chlorine or bromine and are not ozone-depleters, but some (e.g. C_2F_6) have high global-warming potentials. The remaining materials deplete ozone and will be phased out by the year 1996 in developed countries under the Montreal Protocol. Several alternatives are now available while others require further testing and development (Felty 1991).

Mixtures of various fluorocarbons (FCs) and hydrofluorocarbons (HFCs) with nonozone-depleting chlorine sources may be an alternative used in the etching process (see Table IX-4). Some of these (e.g., SF_6, CF_4, C_2F_6, HFCs) may have high global-warming potentials. Many of these alternatives are in the development stages and transition to high volume production with data on cost and impact on production yields have not yet been determined. Adopting any of the other alternatives will require modifying processes to account for variances in reaction kinetics and materials and insuring equipment compatibility. Another factor limiting the attractiveness of these alternatives (Felty 1991) is conversion costs or loss in yields.

One possible option is the use of chlorofluorocarbon (CFC) alternative compounds. Several of the fluorocarbon compounds listed in Table IX-5 are potential replacements for existing CFCs. Many of these compounds have been evaluated as etchants, with some reported success (Mocella 1991). Like the substitutes, some of the materials have no ozone-depleting potential while others, primarily the HCFCs, have low ozone-depletion potentials and may, for a limited time, find uses in critical applications. However, potential users of HCFCs should be aware that these chemicals were recently added to the list of substances controlled under the Montreal Protocol and are currently scheduled to be completely phased out by the year 2030, with a 99.5% reduction required by the year 2020.

9.8.2 Oxide Growth Processing

1,1,1-Trichloroethane is used for silicone oxidation in diffusion furnaces during semiconductor wafer fabrication processing. 1,1,1-Trichloroethane is delivered through a leak tested system to the silicon oxidation furnaces where the following reaction takes place:

$$CH_3CCl_3 + 2\ O_2 \text{ -- } 2\ CO_2 + 3\ HCl$$
$$4\ HCl + O_2 \text{ -- } 2\ Cl_2 + 2\ H_2O$$

It should be noted, however, that none of the 1,1,1-trichloroethane is emitted to the atmosphere. This use is a transformation process and should be treated in the same way as feedstock applications. The combustion reaction is quantitative, whenever sufficient oxygen is present. Even in an oxygen deficient environment, 1,1,1-trichloroethane quantitatively decomposes at the furnace temperature forming carbon, carbon monoxide and HCl. The chlorine species produced as by-products of the diffusion reactions, chlorine and hydrogen chloride gases, are scrubbed to prevent emission to the troposphere.

9.8.3 Semiconductor Degreasing

CFC-113 and 1,1,1-trichloroethane are used in the electronics industry to degrease semiconductors as part of the silicon wafer fabrication process. In the late 1980s, two companies jointly announced the introduction of a new technology for cleaning semiconductor wafers. The technology, called "water-ice cleaning," does not require CFC-113 or 1,1,1-trichloroethane. It relies instead on a spray of ice particles 30 to 300 microns in diameter. The particles are delivered at close to the speed of sound and at temperatures below -50°C. The hardness and size of the particles as well as the pressure

Table IX-3. HALOCARBON PLASMA ETCHANTS

Designation	Formula	ODP
CFC-11	$CFCl_3$	1.0
CFC-12	CF_2Cl_2	1.0
CFC-13	CF_3Cl	1.0
CFC-13Br	CF_3Br	10.0
FC-14	CF_4	0.0
HFC-23	CHF_3	0.0
CFC-115	C_2F_5Cl	0.6
FC-116	C_2F_6	0.0
Carbon Tetrachloride	CCl_4	1.1

Source: Adapted from Mocella 1991.

Table IX-4. POSSIBLE MIXTURES FOR CFC REPLACEMENT IN DRY ETCHING

Alternative 1:	Fluorocarbon	±	Chlorine Source
	CF_4 C_2F_6 CHF_3		Cl_2 HCl $SiCl_4$ BCl_3
Alternative 2:	Fluorine Source	±	Chlorocarbon
	NF_3 SF_6 SiF_4		CCl_4[a] $CHCl_3$

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[a] CCl_4 is an ozone-depleting substance (ODS) and scheduled for a phaseout under the Montreal Protocol.

Source: Mocella 1991

Table IX-5. CFC ALTERNATIVE ETCHING COMPOUNDS

Designation	Formula	ODP
HCFC-22	CHF_2Cl	0.055
HCFC-123	CF_3CHCl_2	0.02-0.06
HCFC-124	CF_3CHFCl	0.02-0.04
HFC-125	C_2HF_5	0.0
HFC-134a	CF_3CH_2F	0.0
HCFC-141b	$CFCl_2CH_3$1.5	0.11
HCFC-142b	CF_2ClCH_3	0.065
HFC-152a	CH_3CHF_2	0.0

Source: Adapted from Lerner, Mocella 1991.

and angle of the spray can be controlled as needed. This process is designed for use in place of the vapour degreasing stage of wafer processing (Nikkei Sangyo Shinbun 1989, Denpa Shinbun 1989).

9.8.4 Photolithographic Processing

The photolithographic process for semiconductor wafer fabrication uses CFCs in various cleaning and drying processes. In semiconductor manufacturing, processes and equipment are designed around various solvents and specific application needs (e.g., chlorine source for etching silicone as part of the photoresist process). The use of lasers and dry photoresist methods or the implementation of aqueous chemistry photoresists can reduce solvent dependency (Karash 1991).

9.9 MISCELLANEOUS TESTING

9.9.1 Leak Testing

Both helium and CFC-113 are being used as an alternative to detect leaks in aircraft fuel tanks. Any solvent compatible with tank materials can be used as a substitute for CFC-113. Helium is being used successfully for leak detection. In detecting leaks in metal gyro housings, for example, CFC-113 is also used as a medium. The integrity of the seal in certain metal gyro housings containing an inert gas atmosphere is tested during repair operations by immersing the housing which contains pressurized gas into a bath of CFC-113. This method quickly locates any "gross" leaks that may exist. Possible alternatives for gyros include replacing the CFC-113 with a blend of cyclic fluorocarbon ether and aliphatic fluorocarbon or with a solution made from pure water and a surfactant. There are also systems available which detect leaks of this type using infrared techniques (Hunt 1991). Perfluorocarbons (PFCs) have associated global warming issues.

9.9.2 Laboratory Testing

CFC-113, 1,1,1-trichloroethane, and carbon tetrachloride are also used for analyses in laboratories or investigations (e.g., quality testing and analyzing oils and greases). Use of ozone-depleting solvents in laboratory applications has been granted a global exemption to the phaseout by the Parties to the Protocol for a period of two years beginning in 1996. Refer to the global exemption and ongoing activity in this area for more information.

9.10 MOULD RELEASE AGENTS

In order to prevent adhesion, release agents form a barrier between a moulding compound and the mould. Sometimes release agents also function as a lubricant and are used in the moulding of graphite epoxy thermoplastic, thermosetting plastic, and rubber parts.

The active component in a release agent may be mixed with the moulding compound (an internal release agent) or sprayed onto the mould prior to moulding (an external release agent). Only external release agents contain solvents. Waxes, fatty acids, silicone oils, or fluoropolymers are normally used as the active component in external release agents. To insure an even application of the release agent, the active component is diluted with solvent to produce a formulation of one to five percent active ingredient and the remainder a mixture of solvents.

Commonly used in the solvent mixture to control both the flashpoint of the release agent and the evaporation rate of the main solvent, 1,1,1-trichloroethane's high density prevents sedimentation of the active ingredients. It is rarely used for its solvent capabilities. Other components of solvent mixtures include xylene, mineral spirits, methyl ethyl ketone, and ethanol. With fluorinated polymer release agents, 1,1,1-trichloroethane swells the fluoropolymer and makes it "fluffy," which counteracts sedimentation and improves the agent's release properties. In release agents with other active ingredients, 1,1,1-trichloroethane does not serve the same function and reformulation should prove simpler.

The recent trend in industry is toward the use of internal release agents or water-based external release agents. Internal release agents, however, are not good for foamed products since the structure of the foam is partially controlled by surface-active foam stabilizers whose function is disturbed by the internal release agent. The plastic foam industry, therefore, is pushing the development of water-based external release agents. The general objection to water-based release agents is that they evaporate too slowly and reduce the temperature of the mould (which then lowers the production rate). Internal release agents are a possible alternative for moulded rubber products.

Several manufacturers of aerosol mould release agents have developed "nonsolvent" formulations in which the active ingredient is dispensed without the aid of a solvent. This type of formulation has proven effective in some applications. A potential problem with nonsolvent mould releases is the uneven dispersion and wetting that can occur because the active ingredient is not solubilized.

9.11 FILM CLEANING

Prior to the introduction of the Lipsner Smith Motion Picture Film Cleaning Machine, film was most often hand-cleaned. A typical cleaning operation would include a solvent-wetted wiping cloth and a set of rewinds. The solvent of choice was carbon tetrachloride (Mertens 1991a, Tisch 1991).

When Lipsner Smith designed the first automatic film cleaning machine, carbon tetrachloride's excellent solvent action, its rapid rate of evaporation, non-flammability, and its lack of any softening action on the film were recognized. Because of known toxic effects, Lipsner Smith investigated alternative solvents and liquids that would provide the same characteristics without the toxicity problem. Some of the solvents evaluated included cyclohexane, hexane, methylene chloride, perchloroethylene, 1,1,2-trichloroethylene, 1,1,2-trichloro-1,2,2-trifluoroethane, and 1,1,1-trichloroethane (Mertens 1991a, Tisch 1991).

1,1,1-Trichloroethane, because of its desirable solvent characteristics, its low cost and low toxicity, was chosen to be used with the mechanized Lipsner Smith system. From that point on, 1,1,1-trichloroethane has been the world's most commonly used film cleaning solvent and is used exclusively with Lipsner Smith machines (Mertens 1991a, Tisch 1991).

With the exception of limited competition in France and Japan, Lipsner Smith machines dominate the world's market for film cleaning. There are approximately 600 users worldwide who use approximately 1,500 units. These users make up an estimated 90 percent of the total units used in the world for film cleaning. The typical Lipsner Smith user is a film laboratory or film-to-videotape transfer facility which operates two units with an annual solvent usage of about 15 drums (55 U.S. gallons/drum) (Mertens 1991a, Tisch 1991).

The film cleaning industry is now rather steady as the film-to-videotape revolution of the 1970s and 1980s appears to have run its course. As a result, the need for film cleaning will continue for the next several years as its only foreseeable replacement technology is coming from high-definition video as an origination medium and/or as a theatrical distribution medium. However, this technology is unlikely to have any significant impact for at least ten years (Mertens 1991a, Tisch 1991).

Since the addition of 1,1,1-trichloroethane to the Montreal Protocol, Lipsner Smith has reviewed their needs and the choice of 1,1,1-trichloroethane as the cleaning solvent. They have tested several alternative cleaning solvents with varying levels of success.

Perchloroethylene is a viable substitute for 1,1,1-trichloroethane in virtually all film cleaning applications. As a result specially designed cleaning equipment has been developed that limits emissions of perchloroethylene during the cleaning process. This special equipment helps to reduce the risks to workers associated with the toxicity of this substitute. Besides the health risks associated with the use of perchloroethylene, users must consider the slower drying time as compared to 1,1,1-trichloroethane. However, while perchloroethylene's lower volatility increases drying time, it decreases solvent consumption because less solvent is lost through evaporation.

Another alternative that has proven effective in select applications is water-based film cleaning. These systems clean film using a spray system and a water/surfactant cleaner formulation. The major concerns with water-based spray cleaning are the potential for damage to the film caused by the spray and the need for a special drying stage in the process.

Two other alternative solvents are currently being evaluated for use in the film cleaning industry -- perfluorocarbons (PFCs) and hydrofluorocarbons (HFCs). Lipsner-Smith has been testing HFC 43-10 and hopes that it can be marketed in the film cleaning sector as a replacement for 1,1,1-trichloroethane in the next one to two years. PFCs and HFCs have global-warming issues which should be taken into consideration during evaluation.

9.12 COMPONENT COOLING

CFC-11 and CFC-12 in aerosol cans are used to cool, or thermally shock, electrical components during certain diagnostic procedures in the fault isolation of defective circuits and circuit components on printed circuit boards. HCFC-22 is an alternative with a much lower ozone-depletion potential

(ODP) which provides essentially the same degree of cooling. However, because HCFC-22 still contributes to ozone-depletion, other alternatives have recently been developed. These include HFC-134a or liquid nitrogen in aerosol cans, as well as mechanical cooling devices using a vortex principle and compressed air (Hunt 1991).

There are other uses of CFC-113 and 1,1,1-trichloroethane such as pre-surgical skin cleaning and as a cooling media in controlled fusion experiments (Stemniski, 1991a). The Committee believes that the quantity used in such uses is small. These uses were not discussed in detail by the Committee.

9.13 MANUFACTURE OF SOLID ROCKET MOTORS

Ozone Depleting Substances (ODSs) have been routinely used globally for decades in the manufacture of space launch vehicle solid rocket motors (SRMs). The primary ODS solvents used are 1,1,1-trichloroethane (TCA or methyl chloroform) and CFC-113. These substances are used because of their excellent cleaning properties, low toxicity, chemical stability and non-flammability. Non-flammability is of critical importance to the safety of operations involving highly energetic propellant materials.

In the United States, large solid rocket motors (SRMs) are used to launch into space communication, navigational and scientific satellites and the manned Space Shuttle orbiters. Large SRMs include the existing Titan IV SRM as well as its upgraded version called the SRMU and the Space Shuttle redesigned solid rocket motor (RSRM).

a. The SRM manufacturing industry is unique in that there is no method to test the performance of an individual SRM prior to use. The only way an SRM can be tested is for it to be static fired. In this way, it is consumed and cannot be used again (although various components may be re-used, as is done in the Shuttle program.) Accordingly, SRM success can only be assured through rigorous manufacturing including detailed material specifications and continuous quality control.

b. SRM manufacturing is also unique in that the physics and chemistry of SRM functioning is currently only partially understood. For example, burning of SRM propellant has not been completely physically modeled or described due to the extremely high temperatures and gas velocities involved. Therefore, the knowledge of rocket manufacturing gained in the past is critically important to safety and reliability. SRM manufacturers can change current methods of manufacturing only after long-term testing and extensive evaluation. Even after such evaluations, it is not certain that the change in methodology will be successful on the SRM. Accordingly, the end users (customers) of SRMs require SRM manufacturers to follow a rigorous system of change control whose objective is to ensure that no changes in the SRM manufacturing process be made without explicit advance approval based upon the results of the extensive testing. Such testing and evaluation can involve numerous steps up to and including full scale ground-level static firing of an SRM.

c. Despite these technical safety and reliability challenges, the SRM industry has successfully tested, approved, and implemented significant ODS elimination. Since 1989, the four US manufacturers of large SRMs have eliminated over 1.6 million pounds of ODS use per year. Current (1994) ODS usage is less than 48 percent of the use in 1989. Usage in 1995 is estimated to be less than 22 percent of 1989, and manufacturers have committed to complete elimination of ODSs within the next few years.

Update on the NASA/Thiokol Applications

The National Aeronautics and Space Administration (NASA) and Thiokol was granted an essential use production exemption for 1996 and 1997. NASA/Thiokol have proceeded with their phaseout and are ahead of schedule for eliminating non-essential uses and investigating additional alternatives and substitutes. However, at this time NASA/Thiokol has not identified any acceptable substitutes that would reduce their essential use below the previously calculated amounts. It is expected that they will request the government of the United States to nominate an extension of essential use for the years 1998, 1999, 2000, and 2001.

Other U.S. Rocket Applications

The Solvents, Coatings, and Adhesives Technical Options Committee (TOC) reported in the March 1994 Report that it was likely that all manufacturers of solid rocket motors use ODSs. The Committee has confirmed that other U.S. and European solid rocket motors use these substances and that these organizations are expected to nominate additional essential uses by January 1, 1995 for decision in 1995.

a. The U.S. Air Force Titan Program may prepare an Essential Use Exemption request for Continued Use of TCA for Critical Titan SRMU Manufacture. A nomination by January 1, 1995 could be considered for Decision by the Parties in November 1995.

b. The Titan launch system offers assured access to space for payloads requiring heavy-lift capabilities. Titan payloads have historically been among the most important and valuable in space exploration, e.g., the Gemini manned space program, Helios solar observers, Viking Mars landers, and Voyager deep space probes. In the near future, Titan will launch Cassini, a fully integrated international exploration spacecraft. Communications, environmental, scientific, and international security satellites are expected to be among the payloads carried into space on Titan in the next decade.

c. The U.S. Titan program is working to completely eliminate the use of ODSs and has invested substantial resources in successfully developing alternatives to ODS use. The original production schedule of the Titan solid rocket motor upgrade (SRMU) required completion of hardware delivery in 1995. At the same time that the amendments to the Montreal Protocol accelerated ODS phase-out requirements, the Titan Program slowed down production to complete hardware delivery in 1999. The combined effect of these two events has made it impossible for the Titan Program to qualify alternatives for all ODS uses by the ODS projection ban of 1 January 1996. It is therefore necessary that small-quantity critical uses of 1,1,1-trichloroethane continue, to allow completion of the currently authorized compliment of Titan SRMUs. These uses cannot be modified without full qualification testing, which would disrupt the launch schedule for years, cost hundreds of millions of dollars, and effectively halt the contributions of the Titan program to global access to space.

d. The Titan manufacturing team has undertaken an intensive program to identify and evaluate alternatives to ODS throughout the rocket motor production process. The program includes eliminating non-critical uses and minimizing the quantities of ODS in essential uses. The prime contractor and the major manufacturers of Titan IV vehicle components will reduce all ODS use by 99 percent, from 1.33 million kg in 1989 to 9,200 kg in 1996. Four small-quantity ODS uses are critical to the success of the Titan SRMU. These are (1) surface preparation to ensure effective bonding of the internal insulator to the composite case, (2) surface preparation to ensure effective attachment of breather cloth to the insulator to permit uniform curing, (3) surface preparation to ensure effective bonding of the propellant to the insulator, and (4) dispersing propellant cure catalyst during propellant mixing. The quantity of ODS necessary to complete SRMU manufacture for the final nine flight sets is 3,660 kg per year or less for 1996 through to 1999.

e. As in the case of the Shuttle Program, substitutes for certain critical uses with severe safety and reliability concerns have not yet been identified or have not yet been qualified. Given this critical need for safety and reliability, the Request for Exemption for continued TCA production to support these essential needs may be submitted. The request, if submitted, will need to contain detailed discussions of the critical needs for continued use, search for alternatives, and future plans to minimize the TCA quantities needed.

European Rocket Applications

The TOC has learned that ODS are currently used in European liquid and solid rocket motors.

a. Both CFC-113 and TCA are used in the European Ariane Espace Program. Efforts to find substitutes for these programs concern CRYOSPACE for liquid rocket engines and Societe Europeenne de Propulsion (S.E.P.) for solid motors.

b. CRYOSPACE will not apply for an essential use exemption this year. Stockpiling and substitution are expected to address their present concerns. S.E.P. is expected to apply for an exemption before 1 January 1995. The processes involved might be slightly different from those of the Shuttle or Titan IV Programs but are also similar because the Ariane rockets carry comparable large payloads. However, given the similar need for safety and reliability it is likely that their exemption will also contain detailed discussions of the critical needs, search for alternatives, and future plans to minimize the ODS quantities needed.

Japanese Rocket Applications

The TOC has learned that ODSs are currently used in Japanese solid rocket motors but an essential use exemption is not expected.

a. Development of Japanese SRM technologies began in 1953. Over 40 years of research as well as trial and error resulted in the development and manufacture of vehicles ranging from sounding rockets and satellite launch vehicles to defense related systems. The Japanese space rocket industry currently uses CFC-113 and TCA but expects to phase out the uses by the end of 1995. Latest achievements include the solid rocket booster (SRB) for the H-II launch vehicle which is capable of launching a 2 Ton satellite to

Geosynchronous orbit. The SRB is 1.8 meter in diameter, 23 meters long and weighs 70 Tons. Two SRBs are attached to the first stage of the two stage H-II vehicle which is 50 meters long and weighs 260 tons.

b. The three stage MV rocket with a 2.5 meter diameter SRM is on schedule in design and construction. The Japanese scientists independently developed specialized materials and manufacturing processes utilizing both metallic and nonmetallic materials. These materials require surface activation of each layer by an advanced shot blasting technique rather that the use of TCA. Phase out of TCA is on schedule for the end of 1995.

c. It is recognized that the Space Shuttle and the Titan IV are significantly larger vehicles relying on previously qualified technologies. Due to their size, design and operational differences and unique performance requirements, the Shuttle and Titan programs have critical uses not required on Japanese launch vehicles. Japanese industry has recommended that Space Shuttle and Titan programs continue to use TCA for critical uses until the schedule allows complete testing of alternatives.

9.14 OXYGEN SYSTEMS CLEANING

In January 1994 NATO identified the cleaning of oxygen systems as one of the most difficult challenges facing military and aerospace applications. In Fall 1994, the International Cooperative for Ozone Layer Protection (ICOLP), Aerospace Industry Association (AIA), U.S. Environmental Protection Agency, National Aeronautical and Space Administration (NASA) and the U.S. Air Force convened a special workshop on cleaning of oxygen systems without ozone-depleting solvents. This section of this report is based on their conclusions and recommendations.

Oxygen systems include: life support systems such as diving, totally encapsulated suits, emergency breathing devices, fire & rescue backpacks, submarine, aircraft, manned spacecraft, and medical applications; propulsion systems such as liquid rocket motors; industrial systems such as chemical production; and other unique systems and customer products such as welding equipment.

Oxygen itself is chemically stable, is not shock-sensitive, will not decompose, and is not flammable. However, use of oxygen involves a degree of risk because oxygen is a strong oxidizer that vigorously supports combustion. Oxygen is reactive at ambient conditions and its reactivity increases with pressure, temperature, and concentration. Most materials, both metals and nonmetals, are flammable in high-pressure oxygen. Therefore, systems must be designed to reduce or eliminate ignition hazards.

The successful design, development, and operation of oxygen systems requires special knowledge and understanding of material properties, design practices, ignition mechanisms, test data, and manufacturing and operational techniques. Oxygen systems must be kept clean because organic compound contamination, such as hydrocarbon oil, can ignite easily and provide a kindling chain to ignite surrounding materials. Contamination can also consist of particles that could ignite or cause ignition when impacting other parts of the system. Risk is increased by the typical proximity of oxygen systems to very large quantities of fuel materials, and the common necessity of locating oxygen systems in confined spaces with difficult or impossible access and egress (e.g. space ships, submarines, aircraft, and surface ships). Despite safety engineering efforts, formal safety requirements and procedures, and cleaning with CFC solvents--CFCs are not the only solvents used--; serious accidents have occurred. These accidents have resulted from a variety of situations including human error, poor design and material selection, hydrocarbon and particulate contamination, and unanticipated circumstances including collisions and acts of war.

The oxygen system cleaning challenge is directly affected by the system's materials, system geometry, location and access, operational parameters, and the type and extent of contamination including cleaning and verification fluid residue. For example, the increased atmospheric pressure in deep diving drastically lowers acceptable human exposure limits for solvent residue.

Examples of the challenges presented by these applications include the cleaning of the space shuttle external fuel tank, cleaning of aircraft carrier liquid oxygen plants, cleaning of installed submarine and transport aircraft high pressure oxygen systems, and the gauges and instrumentation associated with each. Examples of devices typically cleaned in these systems include tubing, gauges, regulators, valves, and metering devices. It is usually most effective to clean oxygen equipment at the piece part level in a proper facility. It is more difficult to clean oxygen equipment in aircraft and ship equipment in place with difficult accessibility and temperature extremes. Additional challenges occur in many other industrial oxygen systems such as those used in production and transfer of both gaseous and liquid oxygen, in medical applications, and in welding. Cleaning of equipment used in the oxygen production industry involves unique challenges such as compatibility with aluminum heat exchangers.

For oxygen systems are expressed in mg per unit area of total contamination (measured as non-volatile residue). These standards are empirically developed and operationally justified for specific applications. They vary from country to country and application to application. In the United States the generally accepted standards of cleanliness for military, aircraft, and hospital applications is 3.0 mg/sq. ft.; for NASA space applications the standard is 1.0 mg/sq. ft.; and for industrial applications it is 10-50 mg/sq.ft. Standards and test methods are specified in American Standard Testing Methods (ASTM-G63 for evaluating nonmetallic materials, -G88 for designing systems, and -G94 for evaluating metal materials), Compressed Gas Association (CGA), Department of Defense (DOD), NASA (SN-C-0005), Society of Automotive Engineers (SAE), and other documents. These standards are empirically developed, operationally justified for specific applications. However, they may be too low or too high for unique applications with atypical conditions such as rapid changes in temperature or pressure or unusual electrostatic potential.

Solvents such as non-ozone depleting chlorinated solvents and hydrocarbons often clean satisfactorily, but all have environmental or toxicity concerns, and some have flammability concerns. Environmental, worker safety, and flammability concerns are addressed when cleaning choices are made for specific systems.

Traditional cleaning with CFC-113 and 1,1,1-trichloroethane (scheduled for production phase-out under the Montreal Protocol) is only sustainable using stockpiles or new production under terms of the Montreal Protocol's Essential Use Process. Historically verified cleaning with chlorinated solvents is possible in some circumstances where worker exposure can be mitigated, but not for applications in confined spaces and for certain life support systems. New solvents such as HCFCs and HFCs may be appropriate for some of these situations, but the problem of performance and safety has not yet been verified for all applications and HCFCs are scheduled for phaseout after 2000.

Aqueous cleaning options have been successfully developed and implemented for many oxygen system cleaning situations. For example, Lockheed uses aqueous processes in the manufacturing and maintenance of aircraft and missile oxygen systems, the Air Force uses aqueous cleaning for some aircraft oxygen system maintenance, NASA/Kennedy Space Center uses aqueous solutions for cleaning oxygen bulk storage and transfer systems for rocket motors, and the U.S. Navy uses aqueous cleaning processes for cleaning the tubing in oxygen systems on ships and submarines.

Aqueous cleaning of oxygen systems often requires enhancement for cleaning efficiency through means such as ultrasonics, increased temperature, spray, or aggressive flushing. The performance of each option must be verified to the particular application. It is also important to verify supplier claims and monitor quality assurance.

Isopropyl alcohol (IPA) is being used by Lufthansa German Airlines to clean the oxygen systems in their commercial aircraft fleet. Sweden has reported using a solvent blend for oxygen system cleaning consisting of 95% ethanol.

Some parts of oxygen systems can be changed to simplify or avoid the necessity of cleaning or they can be adapted to allow aqueous cleaning.

Some oxygen system components still depend on CFC or chlorinated solvent cleaning because current alternatives and substitutes are not technically suitable. In other cases, rigid specifications and requirements may need to be changed from prescriptive to performance standards to allow technically feasible solutions to be used. For example, anodized parts that are dyed for visual identification may fade with certain aqueous cleaning processes. Anodized surfaces have also been attacked by heated aqueous solutions. Components and systems with complex geometries may trap fluid or have voids and spaces where high surface tension cleaners cannot remove soils. Thus, a particular aqueous process will not be appropriate for all situations, but it is possible to select an aqueous system to clean many oxygen systems and sub-systems.

Some parts of oxygen systems can be changed to simplify or avoid the necessity of cleaning or they can be adapted to allow aqueous cleaning. For example:

Option 1: By-pass service ports can be added to equipment to allow pressure gauges to be calibrated in-place rather than through removal and subsequent calibration which increases the chance of gage contamination and system contamination through opening which thus often leads to cleaning.

Option 2: Replace pressure gauges with new gauges at frequent intervals to avoid the current practice of cleaning and calibrating at fixed intervals, thereby eliminating the need for maintenance cleaning.

Option 3: Send the gauges to central cleaning facilities that can use alternative cleaning processes.

Option 4: Replace the difficult-to-clean blind tube bourdon tube gauges with transducer or liquid filled, sealed-tube gauges which are both much simpler to clean. Other changes such as eliminating or changing paint and dyes that are incompatible with aqueous cleaning may also help facilitate cleaning without CFCs.

The selection of any cleaning process requires careful evaluation of toxicity and the possibility of exposure controls, of the new residue that may be introduced by the cleaning fluids, of the suitability of test procedures for quantifying the allowable concentrations of new residues, and of the new challenges of a new cleaning process such as rinsing, removing the bulk chemical or water from the surface of components, and drying.

Screening of substitutes and alternatives also involves cleaning and drying performance, cost, materials compatibility of the cleaner and residues, consideration of worker health and safety, and evaluation of proper disposal of waste soils and cleaners.

Implementation may require re-qualification in the operational environment, careful training of cleaning personnel, effective testing for quality and continuous vigilance to confirm that suppliers meet strict product requirements.

9.15 CORRECTION FLUIDS

Traditionally, 1,1,1-trichloroethane has been used as a carrier for whitener in correction fluids. Currently, formulations are available that use water or petroleum distillates as an alternative.

9.16 FABRIC SPOT REMOVER

In some areas, ODSs such as 1,1,1-trichloroethane and carbon tetrachloride are used as a spot remover for the treatment of fabrics. Alternatives include hydrocarbons and perchloroethylene.

9.17 PROCESS SOLVENTS

Ozone-depleting solvents such as 1,1,1-trichloroethane and carbon tetrachloride are used in the process industries (e.g., pharmaceutical, chlorinated rubber, silicone manufacturing, chlorine production). Some alternatives are available as identified in Appendix I. The sector, however, requires further in-depth review which is planned under the auspices of the United Nations Environment Programme (UNEP) Technical Options Panel.

CHAPTER 10

ALTERNATIVES TO OZONE-DEPLETING SOLVENTS IN DEVELOPING COUNTRIES

10.1 INTRODUCTION

Solvents account for approximately 15% of the ozone depletion potential of chemicals targeted for phaseout under the Montreal Protocol. This category includes CFC-113 (chlorofluorocarbon-113), TCA (1,1,1-trichloroethane; methyl chloroform), carbon tetrachloride, and some HCFCs (hydrochlorofluorocarbons). Most of these solvents are used in the manufacture of electronics products; for precision cleaning; to clean metal parts before further processing; and as carriers for solvating agents, lubricants, adhesives, and specialty coatings.

Progress in achieving the phaseout has been excellent in this sector, given the widespread use of ozone-depleting solvents and the variety and complexity of their applications. Of the various uses, the electronics industry has progressed furthest towards a complete phaseout. Full phaseout for metal cleaning applications is hampered by the large number of small users, many of whom are undercapitalized. In precision cleaning applications, users have been aggressively implementing alternatives. Yet, in some cases, they are still searching for solutions for cleaning precision parts that are especially vulnerable to residues or reactivities, or that have unusually stringent cleanliness criteria.

10.2 SUBSTITUTES AND ALTERNATIVES

Substitutes for CFC-113 and TCA of commercial interest include:

- No-clean electronics
- No-clean metal finishing/fabrication/assembly
- Aqueous cleaning
- Semi-aqueous cleaning
- Hydrocarbons and derivatives or oxygenated organic solvents
- Trichloroethylene, perchloroethylene, and dichloromethane cleaning
- Halogenated aromatics (monochlorotoluene/benzotrifluorides)
- Cleaning with hydrochlorofluorocarbons (HCFC-141b, HCFC-225)
- Cleaning with perfluorocarbons (PFCs) or hydrofluorocarbons (HFCs)
- Cleaning with dibromomethane
- Cleaning with volatile methyl siloxanes
- Supercritical fluid cleaning
- Carbon dioxide snow cleaning
- Plasma cleaning
- Ultraviolet/ozone cleaning

10.2.1 No-Clean Electronics

Eliminating cleaning (no-clean) is the preferred choice of all the options that are available. Its current use is extensive in electronics applications. Moreover it is now becoming available in metals preparation - better lubricants (e.g. ones that can be re-used and re-captured; dry film lubricants) and more efficient processes that permit elimination of, or reduction in, cleaning.

In electronics manufacturing, the adoption of no-clean technology often requires upstream investment to ensure cleanliness. For example, board suppliers to the assembly house, whether captive or contract, must often (depending on board complexity) improve their pre-packaging cleanliness and packaging quality in order to assure that no packaging particulates are dropped on the surface of the board during shipping and handling. This step is necessary because the board will not be cleaned after unpacking. Since the packaging material is normally conductive, contamination on the boards from conductive particles can be deleterious.

Often, there is a need for the installation of precise flux application, along with a need for a corresponding means to measure and control this part of the process. There exists relatively low cost, effective technology for this part of the soldering process, which the International Cooperative for Ozone Layer Protection (ICOLP) has available through Northern Telecom's fluxer and tester design.

Advantages:	This process change eliminates the need for cleaning chemicals - a pollution prevention approach that can lower chemical use and waste production. It is a very simple process that has particular application in the manufacture of consumer electronics. It saves costs and/or is cost competitive.
Disadvantages:	More sophisticated industrial and military products may require stricter adherence to cleanliness standards for board fabrication. Sophisticated products require significant technical expertise. So far, it is mostly used during printed circuit board assembly. In metal working, processing and handling procedures can be improved, which can reduce or eliminate the need for cleaning. Very often, however, either the primary or the secondary soil to be removed is particulate matter. If particulates are one of the soils, no-clean is not an effective technology option. Also, use of the "bare minimum" to maximize effectiveness of vanishing oil causes major risk to tool life. Some tools are very costly. For example, connector tools can run as high as $100,000. Some vanishing oils may have associated volatility or Global Warming Potential (GWP) issues.

10.2.2 No-Clean Metal Finishing/Fabrication/Assembly

Elimination of cleaning steps from the finishing fabrication and assembly areas is a preferred option if applicable. There are several possible opportunities to consider no-clean technologies. In some instances it may be practical to just eliminate one or more of the cleaning steps. This step is practical if a part is cleaned more than once during manufacture or is cleaned again after it is assembled. Another possibility is to utilize alternative processing fluids for cutting, drawing, or machining metal parts.

Vanishing oils are one of these methods. A vanishing oil is a very light weight oil, usually with a very low molecular weight. It evaporates from the part after the cutting or machining operation and before an operation that it might interfere with. An example of this process would be where a part is stamped out and then held in inventory for several hours or even days before it is used in the next operation. The next operation may even enhance the evaporation of the lubricant, such as annealing ovens, or other heated operation. Many of the vanishing oils evaporate quite rapidly (within a few hours), and will therefore not interfere with subsequent machining operations. In some cases, it might be possible to utilize a lubricant that is beneficial for the downstream application, or one that does not require removal. Many ferrous metal working operations clean parts then apply a rust preventative material to the part to inhibit rusting during storage or transportation. It is very possible to eliminate the cleaning operation and use the machining lubricant as the corrosion preventative, or apply the corrosion preventative without cleaning off the lubricant. Usually the part is cleaned again when it is ready to be used in the final assembly. Although cleaning is not always completely eliminated, one or more cleaning operations are eliminated.

Advantages: This process change can eliminate the need for cleaning chemicals - a pollution prevention approach that can lower chemical use and waste production. It is a very simple process that has particular application in many metal finishing applications.

Disadvantages: There may be many hidden costs associated with the use of no-clean technologies. Increased tool wear often occurs with the use of vanishing oils, as they are not very viscous. Also, in many operations, there is a need for clean parts for quality control measurements. If a cleaning operation is eliminated for production, a method of cleaning for testing needs to be implemented.

A second disadvantage is that many manufacturers are required to clean parts to a specification set by the customer. The customer will need to change the acceptance specifications that they are currently utilizing. This can be very difficult in today's environment of quality suppliers and just-in-time manufacturing.

10.2.3 Aqueous Cleaning

Aqueous cleaning uses water as the primary cleaning medium, but often detergents (saponifiers) and other chemicals are added to enhance cleaning performance.

Advantages: Aqueous solvent and added chemicals generally have low toxicity and the cleaning power is good for most soils. Chemical costs are low, and there are lower materials losses compared with other cleaning processes.

Disadvantages: Effluent treatment or recycling may be necessary, and drying needs may require new capital intensive equipment and result in higher energy costs. It is not always possible to use aqueous cleaning on water sensitive substrates or on complex geometries. Aqueous cleaning solvents are more time consuming than other methods. Moreover aqueous cleaning may require more floor space, and it may not be effective on high viscosity linear hydrocarbons, asphaltic, micellar or carbonaceous oils. Strongly corrosive (acidic or basic) aqueous cleaning chemicals can require the use of protective gear to reduce exposure due to acute toxic potential or chronic effects. Also, water consumption can be high - up to 10 gallons per minute (gpm), unless water is recycled, which can be a factor in limited water supply or environmentally sensitive situations.

10.2.4 Semi-Aqueous Cleaning

Semi-aqueous cleaning is also a water-based cleaning process that uses relatively low molecular weight organic chemicals to enhance cleaning performance. Semi-aqueous processes include the addition of chemicals such as terpenes.

Advantages: Semi-aqueous solvent cleaners are generally stronger in solvency than aqueous cleaners because their organic portion aids in dissolving organic contamination. The chemicals used in semi-aqueous processes have low toxicity, although their toxicity can be higher than that of the chemicals used in aqueous cleaning processes. Semi-aqueous processes offer good cleaning power for most soils; waste minimization is possible through water reuse, and residual concentrated wastes can be used as cement kiln fuel. Semi-aqueous solvents exhibit a low vapour pressure, so only small quantities are lost to evaporation.

Disadvantages: All degreasing solvents and the organic constituents of blends are volatile, and may require control measures in accordance with national, regional, and local regulations, as well as corporate policy. These control measures address concerns over environmental, health, and safety issues. Effluent treatment is likely since soluble solvents generally have very high biological oxygen demands (BODs), requiring solvent disposal. Flammability and emulsion stability may be an issue in some cases. The drying requirement are similar to those of aqueous cleaning, possibly requiring new, capital intensive equipment and incurring higher energy costs compared with some other options. It is not always possible to use aqueous or semi-aqueous processes on water sensitive substrates or on complex geometries. Moreover this process may require more floor space, as well as high capital expenditure. Water consumption can range up to 2-3 gpm, which can be a factor in limited water supply or environmentally sensitive situations.

10.2.5 Organic Solvent Cleaning (alcohols, aliphatics, ketones, aldehydes, and blends or C1-C20, hydrocarbons and derivatives)

Organic solvent cleaning provides another alternative to ozone-depleting solvents. Alcohols, aliphatics, ketones, aldehydes, and mixtures of these chemicals can be used. As with other options, they have advantages and disadvantages.

Advantages: Organic solvents have good cleaning power and are comparatively simple to use. Process cleaning times are shorter than aqueous or semi-aqueous cleaning. Most contaminated solvent can be easily filtered and distilled, with proper equipment, for reuse. They are also cost competitive.

Disadvantages: All degreasing solvents and the organic constituents of blends are volatile and may require control measures in accordance with national, regional, and local regulations, as well as corporate policy. These control measures address concerns over environmental, health, and safety issues. Most organic solvents are also flammable and/or combustible. For these reasons, special equipment and facilities may be required to ensure protection of worker health and safety. In these cases, capital intensive expenditures will arise. In addition, precautions for waste disposal are necessary. Some organic solvents are unsuitable for use on plastic parts, and low-volatility solvents are difficult to dry, especially on complex geometries.

10.2.6 Chlorinated Aliphatic Solvent Cleaning (trichloroethylene, perchloroethylene or dichloromethane)

Trichloroethylene, perchloroethylene, and dichloromethane do not deplete the ozone layer and can be used as alternatives for cleaning.

Advantages: These non-ozone-depleting halogenated solvents have potentially high cleaning properties for oils, greases and some other organic soils; they are nonflammable and non-corrosive to most materials; and they are simple to use. They offer low operating costs, and it is sometimes possible to retrofit existing equipment at low cost.

Disadvantages: All degreasing solvents and the organic constituents of blends are volatile and may require control measures in accordance with national, regional, and local regulations as well as corporate policy. These control measures address concerns over environmental, health, and safety issues. In addition, special materials and waste handling practices are necessary. Moreover, good waste management practices should be implemented in order to prevent accidental releases to soils and groundwater, which may result in expensive long-term clean-up costs. Newer vapour-tight machines or equipment with vapour emission controls offer more assurances of worker safety, but at a significantly higher cost. Chlorinated solvents may be unsuitable for use on some plastics. High boiling point solvents (e.g. perchloroethylene) may be uneconomic in vapour degreasing operations due to energy costs.

10.2.7 Chlorinated Aromatic Solvent Cleaning (monochlorotoluene/benzotrifluorides)

Monochlorotoluenes/benzotrifluorides are a new option. They have good solvency properties, but they have a low suggested occupational exposure limit (30 ppm).

Advantages: Monochlorotoluenes/benzotrifluorides have the advantage of good cleaning potential. These chemicals also form miscible solvent blends, and some are nonflammable.

Disadvantages: All degreasing solvents and the organic constituents of blends are volatile and may require control measures in accordance with national, regional, and local regulations, as well as corporate policy. These control measures address concerns over environmental, health, and safety issues. As with the other non-ozone-depleting solvents, there is the possibility of contamination of soils and groundwater from spills and accidental discharges which can result in expensive long-term clean-up costs. Some products, especially if contaminated with soils, may emit highly toxic by-products in the event of accidental fire or incineration. This group of chemicals is not yet authorized in the United States for use as replacements for ozone-depleting solvents.

10.2.8 Hydrochlorofluorocarbons (HCFC-123, HCFC-141b, HCFC-225)

HCFC-123 and HCFC-141b are now sold in most markets. HCFC-225, available in some markets now, will be fully available in 1995, except where expressly forbidden by ozone layer protection legislation. These HCFCs are good cleaners for certain specialized applications and can be blended with other solvents such as alcohol for suitable cleaning performance. The U.S. Environmental Protection Agency (EPA) has banned the use of HCFC-141b as a solvent in all cases effective January 1, 1996. Limited exemptions may be granted for replacement of CFC-113 where no other alternative exists. In Sweden all uses of HCFCs in solvent operations were banned as of 1 January 1994.

Advantages: These HCFCs have cleaning power comparable to CFC-113 and they are nonflammable (in most applications). HCFC-225 shows good compatibility with plastics, elastomers and metals, and has a low ozone-depleting potential (ODP) relative to HCFC-141b (.025-.033 ODP depending on the blend of the ca and cb isomers). HCFC-225 can be used in existing retrofitted cleaning equipment. HCFC-141b also has a low toxicity.

Disadvantages: All HCFCs have the disadvantage of being ozone-depleting substances, albeit with lower ODPs than CFC-113, and thus are transitional substances in some uses. HCFC-141b has a low boiling point, a relatively high ODP (.11) and damages plastics and elastomers. HCFC-225 is more expensive than HCFC-141b. All of the toxicological testings of HCFC-225ca and HCFC-225cb planned under the Programme for Alternative Fluorocarbon Testing (PAFT)-IV were completed by early 1994. Based on these PAFT results, the acceptable exposure limit (AEL) of the commercially available HCFC-225 blend has been set at 50 ppm (8hr-Time Weighted Average) by a manufacturer. All degreasing solvents and organic constituents of blends are volatile, and may require control measures in accordance with national, regional, and local regulations, as well as corporate policy. These control measures address concerns over environmental, health, and safety issues. Special low-emissions equipment, which is now commercially available, is essential for environmental protection and solvent usage cost reasons. Retrofitting of existing equipment to utilize HCFC-225 may require additional freeboard, automated lid and hoist emission controls, and replacement of pump seals to prevent excessive emissions. Because HCFCs are transitional in nature, a second shift from HCFCs to a non-ODS alternative will ultimately be required. It may be more cost effective to move immediately to the non-ODS technology to avoid the costs of changing the cleaning process twice, if possible. Good management of wastes is also recommended!

Important note: HCFC-141b has a high ozone depletion potential (ODP) of 0.11, which is equivalent to the TCA ODP of 0.12, and is controlled under the Montreal Protocol. Future changes may further restrict its use or advance its phaseout dates. HCFC-141b should therefore only be considered as a replacement for CFC-113 in specialized applications where no other alternative exists. It should never be considered as a replacement for TCA.

10.2.9 Perfluorocarbons (PFCs)

Perfluorocarbons (PFCs) are a subject of increased interest over the last year, especially for cleaning precision-engineered parts. An atmospheric lifetime of greater than 500 years means that PFCs have a significant direct global warming potential. The US EPA Significant New Alternatives Program (SNAP) allows the use of PFCs in electronics and precision cleaning applications only where users can prove that, due to performance or safety requirements, no other technically feasible alternative exists. Sweden is reviewing the use of PFCs, as an alternative to ODSs, to be permitted only with waivers after January 1, 1996.

Advantages: PFCs are not ozone-depleting substances and should be allowed for special precision cleaning applications, such as oxygen systems, nuclear triggers, and electromechanical gyroscopes. PFCs are non-flammable and of low toxicity. They are good rinsing and drying agents. Furthermore, they are very stable molecules and will not attack non-fluorine containing substrates.

Disadvantages: On the other hand, PFCs are a poor solvent, thus they must be used with other more effective solvent cleaners. All degreasing solvents and the organic constituents of blends are volatile and may require control measures in accordance with national, regional, and local regulations, as well as corporate policy. These control measures address concerns over environmental, health, and safety issues. PFCs are expensive to purchase and they have an extremely high global warming potential. PFCs should only be used as a transitional substance in special applications. The World Bank may request that project applications using PFCs demonstrate adequate emission reduction capabilities in their equipment. New equipment will usually be required.

Important note: PFCs may be controlled internationally or nationally to protect against climate change. They are not recommended for financing under the Montreal Protocol.

10.2.10 Hydrofluorocarbons (HFCs)

HFC solvents are likely to be commercially available within two years. The key environmental characteristic of concern is their long atmospheric lifetime.

Advantages: HFC solvents are non-flammable and of low toxicity. They are better solvents than PFCs, and their behaviour is analogous to CFC-113 in a manufacturing setting, due to similar physical properties. HFCs are the probable drop-in replacement for the use of PFCs. The availability of HFCs is limited now, but several companies have plans for commercial production soon.

Disadvantages: HFC solvents are likely to be expensive and toxicity testing is not complete. Toxicity of HFCs is expected to vary depending on their chemical structure. Due to low solvency, they may need co-solvents to be used in solvent blends or in solvent/solvent systems. These systems are non-ODS, low-GWP, and of low toxicity. They have moderately long atmospheric lifetimes (approximately 20 to 30 years), thus they have moderately high global warming potentials. All degreasing solvents and the organic constituents of blends are volatile and may require control measures in accordance with national, regional, and local regulations as well as corporate policy. These control measures address concerns over environmental, health, and safety issues.

Important note: May be controlled internationally or nationally to protect against climate change. Not recommended for financing under the Montreal Protocol.

10.2.11 Dibromomethane

Dibromomethane (a component of a proprietary product) is a new substitute that entered the market in 1993. Its cleaning power is yet unproven.

Advantages: Dibromomethane is being offered as a drop-in replacement for CFC-113, which would be an advantage where expensive cleaning equipment is in place.

Disadvantages: Dibromomethane has a relatively high ozone depleting potential (ODP) and its cleaning power is unproven. It is likely to be more toxic than methylene chloride (dichloromethane), have a high probability of forming hydrogen bromide and other toxic substances if near a heat source, and its high boiling point (97°C) renders is an unlikely candidate for use with non-metallic parts. Also, it contributes to photochemical smog. All degreasing solvents and the organic constituents of blends are volatile and may require control measures in accordance with national, regional, and local regulations, as well as corporate policy. These control measures address concerns over environmental, health, and safety issues. Since dibromomethane is an ODS, it should not be listed as an alternative. It is considered unacceptable by the U.S. EPA.

Important note: Dibromomethane is not recommended for financing under the Montreal Protocol.

10.2.12 Volatile Methyl Siloxanes (VMSs)

This is another new substitute that entered the market in 1993. It has been used in the past in cosmetics. It use is of particular interest especially for cleaning silicone-based fill fluids in guidance instrumentation. VMSs should be allowed for special cleaning applications, however their use is expected to be infrequent.

Advantages: VMSs have low toxicity. VMSs are one of the few solvents that are chemically compatible with silicone fluids.

Disadvantages: VMSs are expensive. Controls for flammability may be necessary and some formulations have low suggested occupational exposure limits. All degreasing solvents and the organic constituents of blends are volatile, and may require control measures in accordance with national, regional, and local regulations, as well as corporate policy. These control measures address concerns over environmental, health, and safety issues. They have limited applicability.

Important note: VMSs are not yet proven suitable for financing under the Montreal Protocol.

10.2.13 Supercritical Fluid Cleaning (SCF)

Supercritical fluids, especially carbon dioxide, have been used for more than a decade to selectively remove chemical components from processed foods, coffee, hops, and tobacco. Two of the most common uses are to de-caffeinate coffee beans, and remove cholesterol from eggs.

Advantages: This alternative is environmentally benign. SCFs have liquid-like densities combined with the beneficial transport properties of gases, such as low viscosity and high diffusivity. Also, without surface tension limitations, SCFs can penetrate small spaces and are therefore very useful for cleaning complex geometries. Carbon dioxide is additionally advantageous because it is non-flammable, environmentally acceptable, inert, non-toxic, recyclable, and low in cost.

Disadvantages: Only limited applications have been proven so far. In general, hydrophobic contaminants, such as oils, dissolve well in supercritical CO_2. Hydrophillic contaminants, such as inorganic salts, have little solubility. There are high start-up costs that require extra operator training. Equipment to be used with supercritical fluids is capital intensive because of the high gas pressure required to operate the process.

10.2.14 Carbon Dioxide Snow Cleaning

CO_2 snow is a relatively new cleaning technique that can be used to replace CFC-113 and TCA in a variety of cleaning applications. During cleaning, CO_2 snow is directed toward the contaminated surface. Cleaning occurs as a result of the momentum transfer between the solid CO_2 particles and particulate contamination. The collisions loosen the particulates from the surface, and the gaseous CO_2 sweeps them away.

Advantages: Carbon dioxide snow cleaning is an inexpensive method of removing particulates from surfaces. This is a good replacement for the use of CFC-113 as a dusting agent on optical surfaces.

Disadvantages: Carbon dioxide at ambient pressure does not exhibit good solubility properties and it is unlikely that it could be used as a solvent cleaner. Another disadvantage of carbon dioxide snow is that it is much colder than CFC-113 and may cause moisture to condense from the air onto the part being cleaned. Carbon dioxide has a global warming potential and its use would be a net contribution to climate change unless it has a source that would otherwise be an immediate emission. However, most carbon dioxide is scavenged from emissions and thus makes no net contribution to climate change.

10.2.15 Plasma Cleaning

Plasma cleaning may have benefits in the metal cleaning industry equal to the benefits of "no-clean" processes in the electronics industry. Plasma cleaning, especially oxygen, has been used for many years in the electronics industry for the removal of oxides from electronic components prior to adhesive bonding. In recent years, larger pieces of equipment have been used to remove organic contamination from aircraft wings and mechanical devices.

Advantages: The low pressure process is environmentally sound because the waste products are combustion by-products of the organic contamination, usually of very small quantity. Since the plasma acts like a gas, the cleaning ability is independent of the geometry of the part to be cleaned. Plasma cleaning could be the primary method of cleaning metallic parts in the future. Plasma cleaning is more environmentally sound than the use of aqueous or organic solvents.

Disadvantages: Plasma cleaning cannot be used on components that are plastic, rubber, or contain other carbon-based materials. Also, it is often used with many potentially harmful gases and mixtures which could ionize and recombine to form by-products even more detrimental than the original plasma.

10.2.16 Ultraviolet/Ozone Cleaning:

The ability of ultraviolet (UV) light to decompose organic molecules has been known for a long time, but it is only during the past decade that UV cleaning of surfaces has been explored for commercial applications. UV/ozone cleaning is primarily the result of photosensitized oxidation processes. The contaminant molecules are excited and/or dissociated by absorption of short-wavelength UV light. Atomic oxygen and ozone are produced simultaneously when O_2 is dissociated by the absorption of UV with wavelengths less than 245.4 nm. Atomic oxygen is also produced when ozone is dissociated by the use of the UV and longer wavelengths of radiation. The excited contaminant molecules, and the free radicals produced by the dissociation of the contaminant molecules, react with atomic oxygen to form simpler, volatile molecules such as CO_2, H_2O, and N_2. The UV/ozone cleaning procedure is widely used in cleaning prior to thin film deposition in the crystal industry.

Advantages: The process is environmentally safe, yielding non-ozone-depleting products and, of course, not involving any ozone-depleting substances in the process. The UV/ozone cleaning procedure has been shown to be highly effective in removing a variety of contaminants from surfaces. Examples of contaminant effectively removed from surfaces include human skin oils, cutting oil, rosin mixtures, lapping compound, vacuum pump oil, DC-704 and DC-705 silicone diffusion pump oil, and rosin flux from rosin-core lead-tin solder.

Another advantage is that the process is inexpensive, not requiring elaborate apparatus construction or waste product disposal. Depending on the size of the cleaning requirement, few safety features need to be considered. Commercial equipment is available for smaller applications. The UV/ozone chamber also acts as an excellent storage facility for cleaned substrates, preventing any subsequent organic surface contamination. The procedure produces clean surfaces at room temperature.

Disadvantages: The primary disadvantage to UV/ozone cleaning is that thick contamination cannot be effectively removed from substrates. The optimum result is obtained when thin film contamination is present. This requires pre-cleaning before final cleaning. UV/ozone does not remove particles from surfaces unless these particles are organic in composition. The generation of ozone in the procedure may be a safety consideration, and the apparatus, depending on size, needs to be placed in an exhaust hood or other similar exhausting system.

10.3 TECHNOLOGIES FOR DEVELOPING COUNTRIES

The alternatives to ozone-depleting solvents used by the electronics, precision cleaning, and metal degreasing industries have been ranked in order of greatest commercial interest based on environmental effects and on the possibility of their use in developing countries.

The selection of the alternative should be based on five primary factors. The alternative: 1. should not be an ozone-depleting substance, 2. should enable the enterprise to maintain a product reliability level at least equal to the past methods, 3. should be economical, 4. should not create significant environmental problems, and 5. should not compromise worker or consumer health and safety.

Emerging technologies such as HFCs and VMSs are not recommended for implementation and financing until their toxicity, technical, and economic performances are established. Super critical fluid cleaning (SCF), plasma cleaning, and ultraviolet ozone cleaning are recommended for use and financing under the condition that they can be shown to be cost effective, even though they have low environmental impact, because they are mostly used for specialty applications, and because of specialized engineering and training requirements. Other emerging technology, such as dibromomethane solvents, are not recommended for implementation and financing until they are developed further. Chlorinated solvents should only be used where exposure to workers can be controlled within allowed limits.

In order of preference, then, the alternatives that should be considered for developing countries are:

Tier 1: No-clean, keep-clean
Tier 2: Aqueous/semi-aqueous cleaning
Tier 3a: Organic solvent cleaning (with solvents having toxicities less than non-ozone-depleting halogenated solvents)
Tier 3b: Non-ozone-depleting halogenated solvents
Tier 3c: Organic solvent cleaning (with solvents having toxicities greater than non-ozone-depleting halogenated solvents)
Tier 4a: HCFC-225 and HCFC-123
Tier 4b: HCFC-141b
Tier 5: PFCs

Some comments on each of these alternatives should be considered in deciding which is more appropriate for each cleaning application.

All applications to the Fund that propose the use of aqueous or semi-aqueous cleaning should include funding for recycling, waste water treatment, and drying equipment. Applications that involve the use of organic and hydrogenated solvents should include containment equipment, adequate ventilation control, and/or low emission equipment. The guidelines should include requirements for personnel safety, for example, the use of eye guards by workers who perform the cleaning operation.

10.3.1 No-Clean

No-clean is the recommended option for the manufacture of consumer electronics, and it is a preferred option for the manufacture of more sophisticated printed wiring assemblies. To ensure success however, no-clean processes require skilled operators, increased control of incoming part quality, and superior machinery due to narrow operating windows and time to prove its reliability of hardware produced with the technology.

10.3.2 Aqueous/Semi-Aqueous Cleaning

Aqueous and semi-aqueous cleaning technologies, with proper controls and monitoring, are generally considered to have low environmental impact due to the low toxicity of the constituents. However, poor housekeeping practices, such as unnecessary dumping of the cleaning tanks, can cause these cleaners to have worse effects than would ordinarily be expected. In addition, if effluent is untreated, cleaning solution discharges as well as any hazardous soils could cause environmental problems. In an area with water management or water supply problems, aqueous cleaners may be a poor choice unless efficient water recycling is possible. Aqueous/semi-aqueous formulations should be carefully screened to avoid additives that are toxic to human health or may cause synergistic toxicity in the environment. The use of aqueous or semi-aqueous cleaning should include funding for drying, recycling, and waste treatment equipment.

10.3.3 Organic Solvent Cleaning

Although toxicity can be a concern for some formulations, the principal risk is derived from the high flammability of the more volatile compounds. Such solvents are not appropriate for use in settings with sources of ignition unless appropriate precautions are taken, and proper ventilation and individual protective equipment is used. Similarly, the possibility of soil or groundwater contamination is of concern if proper materials handling practices are not followed. Caution should be used when these solvents are used with sprays, heaters, or ultrasonic equipment.

10.3.4 Non-Ozone-Depleting Halogenated Solvents

Where emission issues are of concern, emission control equipment should be included to meet domestic regulations. Strict adherence to proper industrial hygiene practices is essential where these solvents are used because their worker exposure limits are similar to organic solvents. These chemicals have intrinsic properties that point to the possibility of human health and environmental impacts. However, new equipment, although expensive, is available that can control emissions and therefore significantly lower risks. These chemicals should generally be avoided if poor attention to chemical handling and waste disposal procedures is predicted, since inadvertent spills can lead to unacceptable worker exposure and soil or groundwater contamination. All of these chemicals are associated with high start-up costs due to expensive equipment. On the other hand, non-ozone-depleting halogenated solvents may offer the lowest operating costs since they are the least costly chemicals in the group. However, there is a high risk of contaminating soil and/or groundwater in spite of well engineered and maintained systems. The costs of cleaning up contaminated soil and/or groundwater can be substantial. The Implementing Agencies of the Multilateral Fund (United Nations Development Programme, United Nations Environment Programme, United Nations Industrial Development Organisation, World Bank) should consider the cost of monitoring these projects and the cost of insurance that could pay for cleanup.

10.3.5 HCFC-123, HCFC-225, HCFC-141b, and PFCs

HCFC-225 is very similar to CFC-113 in physical and chemical properties, and can form azeotropes with alcohols. They exhibit good materials compatibility and can therefore be used to replace CFC-113 with few changes in the process. HCFCs-225 has been used in applications where other alternative technologies cannot be applied.

Because of a high ozone depletion potential (ODP), HCFC-141b is never suitable as a substitute for 1,1,1-trichloroethane. It is suitable as a substitute for CFC-113 only when lower ODP alternatives, including HCFC-225, are not feasible. Because HCFCs are transitional in nature, a second shift to a non-ODS alternative will ultimately be required. It may be more cost effective to move immediately to a non-ODS technology to avoid the costs associated with qualifying and changing the cleaning process twice, if possible.

PFCs should only be used in electronics and precision cleaning applications where no other alternative will provide the needed performance. Low loss equipment is available for PFCs and HCFC-141b, and if either must be used, this equipment should be used. PFCs are not likely to be an acceptable substitute for manufacturing processes used in developing countries.

Use practices and local environmental considerations can move a particular chemical either up or down in the selection hierarchy.

10.4 RETROFITS

Retrofits for solvent cleaning applications are not as common as for refrigeration or for foam-blowing. Retrofits should not be allowed except in extraordinary circumstances for adapting solvent cleaning equipment to HCFCs. HCFCs are ozone-depleting substances and should not be recommended for use in retrofits, unless the equipment is very new and is designed to have very low emissions through the incorporation of advanced freeboard designs, chiller systems, and adsorption/recycle/destruction systems. For current users of CFC-113 or TCA solvents as cleaners, the most likely retrofits are to:

Chlorinated Solvents

Retrofit of existing cleaning equipment to chlorinated solvents is generally low cost. The chemical properties are similar to TCA and CFC-113 and chemical costs are significantly lower. Most equipment can be modified to use any of the other chlorinated solvents and meet U.S. Occupational Safety and Health Administration (OSHA) or other worker exposure requirements.

However, it is expensive and more difficult to meet the volatile organic compound (VOC) and Air Toxic requirements. The U.S. Maximum Achievable Control Technology (MACT) standards will require more investment in equipment retrofit than the OSHA standards and possible periodic monitoring, record keeping, and reporting. The cost of the retrofit should include a period of monitoring the vapour emissions of the replacement chemical from the machine, and take into account the costs associated with cleaning up contaminated soil and/or groundwater. In addition, monitoring on a basis which is possible in industrialized countries may be difficult to put into practice in some developing countries.

HCFC-225

Since the physical and chemical properties of HCFC-225 are similar to CFC-113, it can be used in a retrofit application, but is recommended only for applications where other, more environmentally acceptable alternatives are not feasible. However, low loss equipment, which is now commercially available, is recommended due to the relatively high cost of HCFC-225.

HCFC-141b

Due to a lower boiling point and high ozone depletion potential, a retrofit can be expensive. Significant degreaser modifications must be made, such as adding freeboard, chillers, programmable hoists, automatic sliding access ports, and molecular sieves, in order to reduce emissions. Moderately high retrofit costs, combined with higher chemical costs, make HCFC-141b a poor candidate for retrofits. Retrofit to HCFC-141b is not recommended for investment.

Retrofits to aqueous and semi-aqueous cleaning is also possible. Degreaser tanks are sometimes retrofitted for water based cleaners, but this requires extensive engineering redesign and should not be attempted without direct consultation with a qualified equipment supplier. For semi-aqueous processes, the chemical manufacturer must also be consulted.

CHAPTER 11

CASE STUDIES OF PHASEOUT ACTIVITIES

This chapter includes company case studies providing examples of successful programmes to eliminate the use of ozone-depleting solvents in industry. The case studies discuss the evaluation and implementation of materials, alternative technologies, and processes to eliminate the use of CFC-113 and 1,1,1-trichloroethane in cleaning operations. The following 22 case studies are presented in this chapter:

1) **Allied Signal** -- "An Evaluation of Aqueous Technologies at Allied Signal Aerospace Canada (ASAC)" -- A description of the evaluation of various aqueous saponifiers.

2) **AT&T Bell Laboratories** -- "AT&T and the Elimination of Ozone-Depleting Substances" -- A description of the alternative cleaning and manufacturing technologies, as well as no-clean techniques.

3) **Beck Electronics** -- "Semi-Aqueous Equipment Conversion at Beck Electronics" -- A description of the evaluation of more than 20 alternative solvents and the design and construction of custom cleaning equipment. Obsolete vapour degreasers were converted to use the new terpene-based solvent.

4) **Ford Motor Company** -- "CFC Elimination in Electronics Soldering at Ford Motor Company" -- A description of the use of no-clean soldering and nitrogen inertion in electronics manufacturing.

5) **Hitachi** -- "Reduction and Elimination of ODS Solvents at Hitachi" -- A general overview of the different types of alternatives evaluated by Hitachi.

6) **Honeywell** -- "Replacement of Ozone-Depleting Substances in Honeywell Space and Aviation Control Products" -- A description of the use of various alternatives to ODSs including supercritical fluid cleaning, CO_2 snow, perfluorocarbon sprays, water-based sprays, and the use of semi-aqueous processes.

7) **IBM Corporation** -- "ODS Elimination at IBM Austin, Texas" -- A description of the aqueous and no-clean processes implemented in the printed circuit board manufacturing process.

8) **Japan Industrial Conference on Cleaning (JICC)** -- "The Japan Industrial Conference on Cleaning" -- A description and history of the JICC, an information clearinghouse formed to assist Japanese industry in identifying and evaluating non-ODS solvents.

9) **Lockheed Sanders Company** -- "The Elimination of 1,1,1-trichloroethane in Electronics Cleaning at Lockheed Sanders Company" -- A description of the alternative cleaning systems employed to replace 1,1,1-trichloroethane use in electronic component cleaning.

10) **Miljoministeriet** -- "Hydrocarbon Dry Cleaning at Miljoministeriet" -- A description submitted by the Danish EPA of the use of an alternative hydrocarbon dry cleaning system to replace ODS use in dry cleaning.

11) **Minebea Company** -- "Phasing Out of Ozone-Depleting Substances by the Minebea Co." -- A description of implementing an aqueous cleaning system for the cleaning of ball bearings.

12) **National Semiconductor** -- "Elimination of ODSs at National Semiconductor, Malaysia" -- A description of management and technical process from team development through implementation.

13) **Naval Aviation Depot** -- "Elimination of Ozone Depleting Solvents at Naval Aviation Depot Cherry Point" -- A general discussion of the program including a special discussion of hand-wipe cleaning.

14) **Northern Telecom** -- "Northern Telecom and CFC-113 Elimination" -- A summary of the steps to eliminate CFC-113 from the program's inception in 1987 and including a discussion of the company's efforts to assist developing countries through cooperation with ICOLP and UNEP.

15) **Robert Bosch Corporation** -- "Replacing Solvent Cleaning with Aqueous Cleaning" -- A case study prepared by the Centre for Aerosol Technology detailing elimination of CFC-113 and trichloroethylene at Robert Bosch Corporation.

16) **Rockwell International** -- "Use of a Low-Residue Flux in a Military Electronics Program" -- Qualification of a low-residue flux on the Hellfire Missile assembly line.

17) **Seiko Epson Corporation** -- "The Cleaning Center System of Seiko Epson Corporation" -- A description of an information clearinghouse and a central cleaning facility to assist small and medium-sized facilities in identifying and evaluating alternatives to ODSs.

18) **Singapore Institute of Standards and Industrial Research (SISIR)** -- "The ODS-Free Verification Scheme for Singapore Industry" -- A description of the SISIR certification of businesses as "ODS-Free."

19) **Swedish EPA** -- "Eliminating the use of ODSs in Sweden" -- A discussion of the programmes sponsored by the Swedish EPA (SNV) to phaseout ODSs in Sweden.

20) **Toshiba Corporation** -- "Non-ODS Substitutes for Wax Elimination at Toshiba Corporation" -- A description of the qualification and implementation of a vinyl-copolymer-type masking agent to replace wax masking in plating applications at aircraft maintenance facilities. Unlike wax, the new masking agent can be removed without the use of solvents.

21) **U.S. Air Force Aerospace Guidance and Metrology Center** -- "Using New Technologies to Solve Unique Precision Cleaning Operations: The Elimination of Ozone-Depleting Solvents at the Aerospace Guidance and Metrology Center at Newark Air Force Base" -- A description of the non-aqueous alternatives used to eliminate the use of ODSs in precision cleaning applications. Alternatives

addressed include alcohols, volatile methyl siloxanes, supercritical fluids, and perfluorocarbons.

22) **Vibro-Meter SA** -- "The implementation of Water-Based Cleaning at Vibro-Meter SA, Switzerland" -- A description of the implementation of a water-based cleaning system to remove flux residues from printed circuit assemblies used in vibration detectors. Includes a brief evaluation of other alternatives considered.

ALLIED SIGNAL - AN EVALUATION OF AQUEOUS TECHNOLOGIES

I. INTRODUCTION

In response to the Allied Signal corporate mandate to eliminate the use of all Class I ODSs from its cleaning operations, Allied Signal Aerospace Canada (ASAC) chose to develop a saponified aqueous replacement process. The project was undertaken in conjunction with recommendations made by the Electronics Defluxing Alternative Team (EDAT), comprised of scientists and engineers from various Allied Signal Aerospace divisions throughout the United States and Canada.

II. EVALUATING METHODS

A total quality leadership-style (TQL) approach was used, whereby a team of manufacturing engineers representing all facilities were responsible for the evaluation of various alternatives. The EDAT classified potential alternatives into three categories: those available for immediate incorporation, those not as readily available and those that would not be considered. The team evaluated three cleaning technologies for immediate use: semi-aqueous, saponified aqueous, and fully aqueous. EDAT used the Index of Technical Feasibility as an analytical measure ranking all weighted technical factors against the relative net present value including life cycle costs to evaluate each alternative. The final selections were based on tests performed on 28 cleaner technology/equipment combinations. Of these combinations, 8 semi-aqueous, 14 saponified aqueous and six fully aqueous combinations of batch and in-line equipment were considered. The controls were CFC-113 and methyl chloroform solvent baseline processes.

A standard and controlled evaluation protocol was developed for all phases of testing. The standard test protocol was based on IPC-CP-61. The amount of ionic contamination on 331 test specimens was determined in accordance with IPC-TM-650, Method 2.3.26.1. In addition to the commonly used visual and ionic testing, EDAT evaluated numerous samples using high-performance liquid chromatography (HPLC), surface insulation resistance (SIR) and ion chromatography tests. The SIR test was performed on 306 of the standard test specimens in accordance with IPC-TM-650, Method 2.6.3.3, Class III. A total of 10,710 SIR readings were taken from seven SIR test patterns on each board, with five readings per pattern. The specific attributes EDAT required for the SIR tests included:

- the results should be as good as or better than the baseline controls
- resistance readings not less than 10^8 ohms
- the difference between initial resistance readings and the first readings at temperature and humidity should be less than LOG 3.

The SIR and HPLC tests were used to identify residual organic residue. The ion chromatography test measured residual ionic contamination and classified them as a chloride, bromide, nitrate or a weak organic acid. Adhesion testing was carried out with acrylic and urethane coatings on 108 of the test boards. Extensive wash and rinse water analyses were conducted and testing was completed for a minimum number of parameters, including lead, BOD (biological oxygen demand) and pH. The EDAT also completed cost analyses for all of the candidate processes. The cost analyses considered capital outlay, installation costs, and operation and maintenance costs.

III. EVALUATION RESULTS

The evaluation of the test results was performed in three phases. Phase I included candidates available for immediate use, Phase II involved detailed tests using various equipment alternatives and the best chemistries identified in Phase I, and Phase III addressed additional chemistries using the equipment selected in Phase II. The SIR data was given the most weight in test evaluations primarily because EDAT believed that SIR tests were the most realistic indicator of long-term reliability. Final test results revealed that two aqueous saponifiers best satisfied the test criteria: an inorganic-based aqueous saponifier with a moderate pH and an organic-based monoethanol-amine (MEA)/glycol ether-based aqueous saponifier. The inorganic-based aqueous saponifier performed effectively and had human and environmental safety advantages. These advantages were the primary reasons for its implementation at the Commercial Avionics System Division. Although the inorganic-based aqueous saponifier is used in a 10% concentration versus a 4% concentration for the organic-based cleaner, its extended bath life makes it a more economical cleaner. In addition, the inorganic saponifier is less aggressive on solder masks than other saponifiers that have a tendency to remove dry-film solder masks. Finally wastewater analysis confirms that the use of inorganic-based saponifiers reduces wastewater contamination, thereby reducing water treatment costs.

Overall, testing of the aqueous saponifiers reveal that both perform better than the benchmark used in the EPA/DoD/IPC Ad Hoc Phase II testing.

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ELIMINATING OZONE-DEPLETING SUBSTANCES AT AT&T

I. SUMMARY

AT&T became a corporate leader in the research and development of alternatives to ozone-depleting solvents. At AT&T, ODSs were used as solvents in a variety of processes ranging from metal degreasing to circuit board fabrication, circuit board assembly, multi-chip module assembly, and semiconductor manufacture. This product variety made AT&T's ODS elimination efforts more difficult than at a less vertically- integrated company. AT&T was able to eliminate ODSs by using its research and development strengths and manufacturing expertise at Bell Laboratories to develop alternative technologies. Also critical to the success of the company's efforts were factory teaming and management support and commitment.

Since developing its alternative technologies, AT&T has expended significant effort sharing its technology with other companies. AT&T, Northern Telecom, and U.S. EPA formed with six other founding companies to support these goals, the International Cooperative for Ozone Layer Protection (ICOLP).

II. INTRODUCTION

AT&T began developing and testing water-soluble fluxes in the early 1980s with good success. In 1988, the company astounded the world when they organized a press conference with U.S. EPA to announce they had co-developed a terpene-based solvent to replace CFC-113 in some processes. Until then, it was argued that CFC was essential to electronics manufacturing. The following year, AT&T developed a precision spray fluxer for use with low-solids (no-clean) fluxes. The same year AT&T announced its goals for aggressively eliminating ODSs as part of a comprehensive pollution prevention plan.

In 1990, AT&T reaffirmed its commitment to the environment by eliminating the use of CFCs in its packaging materials. This and prior actions led to public recognition, including two awards: The American's Corporate Conscience Award from the Council on Economic Priorities, and a U.S. Environmental Protection Agency (EPA) Stratospheric Ozone Protection Award. The following year, additional public recognition for the company's environmental efforts included the New Jersey Governor's Award for Outstanding Achievement in Pollution Prevention, the National Association for Environmental Management's Environmental Excellence Award, a citation in the first President's Environment & Conservation Challenge Award, and another EPA Stratospheric Ozone Protection Award. AT&T also completed development of a water-soluble flux suitable for military applications in 1991.

AT&T has continued to aggressively research and develop alternatives to ODS from 1992 to present. Some of the recent developments include:

- a technique for manufacturing integrated circuits using a non-ozone-depleting solvent;
- a water-soluble solder paste comprised of common food ingredients; and
- a low-residue soldering iron technology.

AT&T eliminated about 1.1 million kg of CFC emissions from its manufacturing operations worldwide by year-end 1992. This action resulted in millions of dollars in manufacturing cost savings. Also during 1992, AT&T was awarded its third U.S. EPA Stratospheric Ozone Protection Award and shipped its 100th low-solids spray fluxer. In 1993, AT&T announced that it had virtually eliminated ODS emissions from its manufacturing operations.

III. ODS ALTERNATIVES

AT&T investigated many types of options to replace ODS use, including:

- alternative cleaning technologies;
- no-clean technologies; and
- alternative manufacturing technologies.

The implementation of all of these options was needed in order to successfully eliminate its use of ODSs because of the great variety of applications in which ODSs were used.

Alternative cleaning technologies

AT&T found that it could change the flux or the solvent used and still obtain acceptable product quality for many of its processes. Technologies implemented included water-soluble fluxes and terpene-based solvents.

Water-soluble flux. AT&T was one of the first companies to implement water-soluble fluxes and aqueous cleaning processes. First initiated in 1981, AT&T continues to use this method in the manufacture of some circuit boards. In 1993, AT&T developed a new family of solder pastes using common U.S. Food and Drug Administration-approved food ingredients to create a water-washable solder paste that is more benign and easier to use than previous water-soluble formulations.

Terpene-based solvents. AT&T worked with Petroferm, Inc. to develop a solvent to replace CFC-113 for circuit boards that could not be cleaned with water alone. The companies completed development and testing of a cleaning solution called BIOACT(R)-EC7 in early 1988. Since this solvent was derived from oranges, it was biodegradable and could be safely handled by a conventional sanitary waste treatment facility.

No-clean technologies

AT&T, working cooperatively with ICOLP and other companies, also investigated the option of using low-residue, low-solids fluxes to eliminate the need for post-solder cleaning altogether.

Low-solids spray fluxer. In 1989, AT&T already had implemented its patented system in its factories, and thus eliminated the need to clean electronics circuitry after soldering. This system controls the application of low-solids flux coatings on circuit boards through precision spraying. As a result, little post-solder flux residue remains and cleaning is unnecessary. In 1994, this technology is being used by AT&T and more than 40 other companies worldwide.

Low-residue hand soldering. AT&T developed a hand soldering iron that greatly reduces the residue from cored-solder wire. It then licensed the technology to Hexacon Electric Company so that others could use this no-clean technique.

Alternative manufacturing technologies

AT&T investigated whether certain products could be manufactured using a different process altogether in order to avoid cleaning methods using ODSs. The company developed alternative manufacturing methods for two of its products -- printed circuit boards and integrated circuits.

Printed circuit board fabrication. During the manufacture of printed circuit boards, a photoresist technique has been used to develop the pattern of conductors on the board. This process originally used chlorinated solvents but now uses an aqueous solution developed by AT&T, eliminating usage of millions of kilogrammes of ozone-depleting and non-ozone-depleting chlorinated solvents.

Integrated circuit fabrication. In early 1993, AT&T scientists and engineers announced that they had developed a new technique for the manufacture of densely packaged integrated circuits (multi-chip modules). The new process used n-butyl butyrate (a common non-toxic chemical) instead of 1,1,1-trichloroethane. N-butyl butyrate is a chemical that occurs naturally in cantaloupes and other fruits.

IV. RESULTS

AT&T applied each of these technologies as early as feasible to achieve its ODS elimination goals. AT&T's ODS emissions had been reduced 86 percent by year-end 1992, with 100 percent elimination at 20 of 44 majority-owned AT&T plants. AT&T had virtually eliminated ODS emissions from all manufacturing by April 1993. Not only did this have environmental benefits, but it resulted in cost savings and yield improvements in many manufacturing processes.

V. TECHNOLOGY SHARING

AT&T's technologies to replace ODS use are available for use by electronics manufacturers worldwide. In addition to developing unique alternative technologies, AT&T has participated in a number of industry cooperatives, several of which have successfully formed partnerships with government to further the dissemination of information on alternative technologies.

To help others address the ODS issue, AT&T founded or participated in the following initiatives:

- **ICOLP.** A cross-industry organization, the International Cooperative for Ozone Layer Protection (ICOLP) is dedicated to sharing knowledge about ODS substitutes with manufacturers worldwide, especially in developing countries that lack resources to research and develop their own alternatives. ICOLP created OZONET, a database of technical options to replace ODSs that is accessible from more than 750 cities in 35 countries.

- **GEMI**. The Global Environmental Management Initiative (GEMI) fosters environmental excellence by businesses worldwide. It coordinates initiatives with academia, government, and non-governmental organizations.
- **UNEP**. AT&T scientists have participated in the first, second and third Solvents, Coatings, and Adhesives Technical Options Committees for the United Nations Environmental Programme (UNEP). The committees evaluate the alternatives to ODSs for cleaning applications and forward recommendations to the signatories to the Montreal Protocol.
- **Environmental Management Roundtable**. This forum for senior environmental officers of major U.S. companies meets regularly to transfer technologies and information.
- **Ad Hoc Solvents Working Group**. This group is a U.S. EPA, U.S. Department of Defense, and industry partnership to qualify ODS alternatives for military applications. AT&T chaired the Testing, Monitoring and Validation Committee.

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SEMI-AQUEOUS EQUIPMENT CONVERSION AT BECK ELECTRONICS

I. SUMMARY

Beck Electronics manufactures electronic products including professional telecommunications and avionic systems. Many of its production lines shared a central CFC-113 cleaning facility. As a result, Beck engineers sought a solvent-type technology which would minimize disruption of production. After evaluating many types of technologies, Beck decided on terpene-based solvents in conjunction with water rinsing. Since terpene-type degreasers were not yet commercially available, Beck retrofitted two vapour degreasers to use terpene-based solvents.

II. INTRODUCTION

Beck's product line includes Electro-Magnetic Interference (EMI) filters for use in Electro-Magnetic Compatibility (EMC) applications, whose typical end uses include telecommunications and avionic systems. Since the central CFC-113 degreasing facility serviced over 1,500 different types of products, Beck preferred to find a technology as close as possible in operation to CFC-using cleaning equipment in order not to interfere with the many manufacturing processes dependent on solvent cleaning. "No-clean" technologies were ruled out.

The general-purpose nature of the facility also meant that the new solvent had to be compatible with the polymer resins and lacquers used in some products, yet aggressive enough to clean even "baked-on" flux residues. Beck also strove to avoid any new process that would have a significant environmental impact, such as technologies resulting in the generation of wastewater.

Beck's first step was to test twenty different alternative solvents. Those solvents formulated around citrus- or pine-derived terpenes had the best results in terms of both compatibility and effectiveness. Unfortunately, equipment specifically built for these solvents was not commercially available at the time.

Time was critical due to the impending deadline set by the Montreal Protocol. Beck's solution to this dilemma was to build its own equipment by converting old vapour degreasers already in its possession.

III. DESIGN CRITERIA

Beck chose to use terpene-based solvents with a water rinse because of the large amounts of soil to be removed and the need to remove ionic contamination. However, since terpenes are insoluble in water, the first stage of rinsing required emulsification of the solvent to allow rinsing by successive water stages. Ultrasonic agitation assisted in forming the emulsion. Beck also found that the terpene-based solvents were most effective when heated to about 40° C, and that overheating would lead to early deterioration of the solvent and would pose a fire hazard. To avoid the generation of wastewater, Beck also required a method to separate the emulsion so that the soil and spent solvent could be isolated for removal and disposal or recycling.

IV. PRACTICAL SOLUTION

Beck had two older two-stage vapour degreasers, one of which had an ultrasonic compartment that was ideal for the emulsification process. However, simply filling the other (sump) side with the terpene-based solvent was not practical because direct heating meant that the solvent in contact with the heating element would become too hot. Beck decided to try an indirect heating approach.

To heat the solvent, A stainless steel tank purchased from a local catering equipment store was suspended in the sump, which also contains emulsified solvent. A pump was connected between the sump and the ultrasonic side of the degreaser so that the hot emulsion could be circulated over the weir between them. In this way, the sump containing the solvent was heated by contact with the emulsion.

A stainless steel solvent tank, purchased from a local catering equipment store was suspended in the sump, which also contains emulsified solvent. A pump was connected between the sump and the ultrasonic side of the degreaser so that the hot emulsion could be circulated over the weir between them. In this way, the solvent in the new stainless steel tank was heated by contact with the emulsion.

The second vapour degreaser was used to perform the final water rinses. Initially, tap water was used. However, Beck soon converted to deionized water to control ionic contamination. The deionized (DI) water is circulated through a carbon filter and resin filter. A later refinement was to circulate the solvent and emulsion through particulate filters to prolong their usefulness.

V. PROJECT SUMMARY

- **Solvent**: Terpene-based.
- **Solvent compartment**: Inner compartment suspended in existing sump tank of vapour degreaser. Indirectly heated to about 35° C. Circulated through particle filter.
- **Emulsion compartment**: Directly heated to about 40° C using existing heaters. Ultrasonic capability of vapour degreaser aids in emulsification. Emulsion circulated over weir, around solvent tank, and returned through particle filter.
- **Rinsing method**: Deionized (DI) water at ambient temperature.

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CFC SOLVENT ELIMINATION IN ELECTRONICS SOLDERING AT FORD MOTOR COMPANY

I. INTRODUCTION

The strategy to eliminate chlorofluorocarbon (CFC) solvent cleaning from Ford Motor Company's electronics printed circuit board manufacturing processes was based on the international recognition of CFC environmental concerns. The successful implementation of CFC-free soldering technologies was the result of developing and applying innovative manufacturing processes. Ford Motor Company became a leader in inert gas wave soldering and eliminated CFC cleaning processes ahead of the schedule mandated by the Montreal Protocol. With the cooperation of the United States Environmental Protection Agency and members of the International Cooperative for Ozone Layer Protection, worldwide technology sharing was accomplished to expedite the CFC/ozone depleting solvent elimination program. This case study will highlight the technical, environmental, and managerial success Ford achieved as a result of accelerating the implementation of the Montreal Protocol.

II. CLEANING OPTIONS

The first steps taken to eliminate CFC/ozone depleting solvent cleaning were to research potential technologies, develop the most viable options, and test these alternatives for reduction/elimination potential. The possibilities were numerous, with each technology providing advantages and disadvantages. The field was narrowed to five possible solutions: No Clean Flux, Inert Nitrogen Soldering, Aqueous Cleaning, Semi-Aqueous Cleaning, and Hydrochlorofluorocarbon Solvent Cleaning. A study was conducted to identify key elements of each technology for feasibility to existing Ford manufacturing plants worldwide. This study highlighted each technology for its effectiveness in eliminating CFC solvent cleaning. Some key areas considered were printed circuit board cleanliness, product reliability, equipment reliability, environmental impact, and cost competitiveness. The selection was narrowed to two technologies that rated highest in these categories: No Clean Flux and Inert Nitrogen Soldering. The implementation of these two technologies provided the best solution for CFC/ozone depleting solvent elimination, but required significant development and testing.

The following list highlights the advantages and disadvantages each technology presented for worldwide implementation:

No Clean Fluxes

Pros:

- Uses existing solder systems
- Lowest cost
- Eliminates CFC emissions
- Reduces volatile organic compound emissions
- Eliminates cleaning machines
- Shortest implementation lead time
- Reduces material usage

Cons:

- Requires new application/control equipment
- Need to determine solder quality
- Need to determine probe test capability
- Need to determine conformal coat compatibility
- Need to determine product long term reliability
- Need to determine component solderability

Inert Nitrogen Soldering

Pros:

- Flux with low solids used
- Best printed circuit board cleanliness
- Probe test easily
- Conformal coats easily
- Eliminates CFC emissions
- Reduces volatile organic compound emissions
- Eliminates cleaning machines
- Reasonable implementation lead time
- Improves product quality
- Reduces material usage -- flux and solder
- Requires less floor space

Cons:

- Additional costs for cryogenic nitrogen and equipment
- Replace existing solder equipment
- New handling procedures for chemicals
- Need to determine equipment emissions
- Need to determine product long term reliability
- Need to determine component solderability
- Need to determine solder quality

With the completion of extensive field, laboratory, and manufacturing plant testing, the new process merged both technologies with superior results. Solder quality was enhanced with cooperation of component suppliers providing improved solderable components to meet the new requirements of the lower activity fluxes used for inert nitrogen soldering. Flux formulations were developed using low activity organic acid without rosins or resins added. Product long term reliability was proven in fleet vehicles and extensive laboratory life tests with 100 percent compliance. Equipment emissions were eliminated for CFCs (100 percent), and formic acid (100 percent), and reduced for volatile organic compounds (70 percent) and lead (40 percent). Printed circuit board probe testing without cleaning was tested and implemented. Conformal coatings without volatile organic compound content were developed with suppliers to eliminate process emissions. CFC cleaning machines were removed from the production floor, which resulted in extra floorspace. Flux material usage was reduced to 80 percent with flux thinner purchases completely eliminated. Flux density test/control equipment was removed from the process with new spray technology and handling procedures. End-of-line ionic contamination equipment was removed from the process with new cleaner solder process stability. New inert wave solder equipment innovations were developed with suppliers to reduce solder joint defects to less than 10 ppm. Finally, capital equipment expenditures were recovered and resulted in additional long term savings in materials consumption, quality products, and equipment reliability.

III. BENEFITS

The elimination of all CFC cleaning on May 1, 1993, for Ford Electronics facilities, exceeded the timing of the Montreal Protocol. In addition to realizing the benefits of CFC emission elimination programs, Ford Electronics embarked on a policy of waste minimization for all sources. This internal requirement to minimize emissions to the fullest extent technically possible resulted in lower emissions in areas not covered by the Montreal Protocol. Volatile organic compound reductions resulted from new equipment developments, material developments, and process parameters that reduce solvent emissions at the source. The ultrasonic fluxer technology eliminated the need to use containment equipment to capture flux volatiles. The 100 percent solids conformal coatings eliminated the emissions of solvents during cure time. The use of inert gas in soldering reduced the content of lead oxides being formed as waste in emissions. Finally, process enhancements eliminated the use of formic acids in the solder process.

IV. CONCLUSION

Ford has shared the knowledge gained from its successful program. Ford's involvement with the International Cooperative for Ozone Layer Protection has resulted in supporting and presenting technical papers at international conferences. This commitment increases the technical knowledge of the electronics industry in CFC elimination strategies. Ford has supported government/industry publications that benchmarked prior cleaning effectiveness and set the path for emerging replacement technologies. This global responsibility, with the help of the United States Environmental Protection Agency, has produced outstanding results and achievements for Ford Motor Company and others.

The success of this program was highlighted by awards presented to Ford's electronics operations and its employees from various sources. The United States Environmental Protection Agency and the International Cooperative for Ozone Layer Protection recognized Ford's contributions, as did the State of Pennsylvania. Various employees have won awards from Ford for their contributions.

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REDUCTION AND ELIMINATION OF OZONE-DEPLETING SOLVENTS AT HITACHI

I. INTRODUCTION

Industries in Japan were requested to switch the usage of trichloroethylene and tetrachloroethylene to 1,1,1-trichloroethane in the late 1980s. Hitachi adopted this policy and changed its systems to 1,1,1-trichloroethane in 1989. Hitachi began to reduce usage of CFC-113 in 1988 by introducing recovery and recycling systems. The company has been steadily reducing its consumption of ozone-depleting solvents since 1989. Hitachi completed its phaseout of CFC-113 in 1993, and 1,1,1-trichloroethane will be phased out in 1994.

The company became a member of the International Cooperative for Ozone Layer Protection (ICOLP) to support this belief. It also sent experts to many ODS phaseout strategy meetings and seminars, with a special focus on those held in developing countries.

Hitachi produces several kinds of products, including electric power generators, electricity transmitting equipment, computers and peripherals, communication equipment, trains, semiconductor devices, and domestic appliances. Alternative cleaning technologies considered to replace ODS solvents for each of these products are described in this case study.

II. ALTERNATIVE TECHNOLOGIES

Hitachi was accustomed to using solvents in cleaning applications and initially focused on solvent-type alternatives, including:

- Hydrochlorofluorocarbons (HCFCs);
- Perfluorocarbons;
- Alcohols;
- Aliphatic Hydrocarbons
- Ketones;
- Ethers; and
- Aromatic Hydrocarbons.

CFC-113 and 1,1,1-trichloroethane are very effective solvents for which Hitachi found no equivalent solvent-type replacements to meet its cleanliness and material compatibility needs. HCFC-225 was initially considered by Hitachi to be similar enough to ODS solvents be a drop-in replacement. However, the Montreal Protocol was amended in 1992 to include the phaseout of HCFCs by the end of 2030, so Hitachi considered this chemical a temporary solution at best and did not actively pursue its use.

Subsequently, many types of non-solvent cleaning and no-clean substitutes were investigated in an attempt to match the cleaning ability of the ODS solvents. Hitachi considered the available alternatives including:

- No-clean technologies, e.g., evaporating oil, lubricant coated steel sheets, thin polymer peeling sheets, and ultrasonic plastic deformation;
- Mechanical cleaning, e.g., blasting and pressurized gas;

- Aqueous cleaning, e.g., alkaline cleaners, hydrocarbon/surfactant cleaners, and steam distillation under vacuum; and
- Miscellaneous options, e.g., ultraviolet light/ozone cleaning, supercritical cleaning.

Based on its investigation, Hitachi established internal guidelines for the selection of alternative chemicals and technologies. These guidelines are:

- No-clean technologies are recommended.
- Chlorinated solvents are generally prohibited, including HCFCs. However, HCFC-225 may be appropriate at times, but only for transitional use.
- Low-boiling point PFCs are restricted.
- Energy consumption of alternative technology is a prime consideration.

The remainder of this case study presents some of the options considered which were eventually adopted by Hitachi.

No-Clean Technologies

Hitachi considered the following no-clean alternatives to reduce its use of ODS solvents:

- lubricant coated steel sheets;
- drying press oil; and
- ultrasonic plastic deformation in pipe working.

The use of lubricant-coated steel sheets was one of the no-clean options considered. In conventional metal pressing applications, lubricating oil is applied and the oil is cleaned off after working the metal. The drawing characteristics of lubricant-coated steel sheets are the same as non-coated steel sheets.

Drying press oil was a second no-clean alternative evaluated. Conventional lubricating oil for punch working is not volatile and the oil must be cleaned off after working the metal. Recently, volatile lubrication oil has been developed which generally leaves minimal residual oil film thicknesses after only one hour drying time at room temperature. Film thicknesses can be reduced even faster at higher temperatures, but a drying furnace is recommended for the fastest drying. It is important to note that some of these drying oils contain chlorinated solvents and require that special attention be paid to occupational health and safety.

Ultrasonic plastic deformation in pipe working was the final no-clean option considered. When ultrasonics are used in plastic deformation processes, it is known that changes occur, including:

- reduction of deformation resistance
- reduction of friction between tool and work piece
- physical and mechanical property changes in metal
- temperature increase in metal.

Since the deformation resistance and friction between tool and work can be reduced, some pipe working can be accomplished without lubricating oil. In the case where the thickness of the pipe wall is not large, the pipe wall will be bent or expanded without lubricating oil

Blasting technology

Some types of residue can be cleaned from work pieces by blasting solid particles at the work surface. When flammable solid particles are used, careful attention must be paid to avoid combustion.

Aqueous cleaning and wastewater treatment

In aqueous cleaning at Hitachi, typically, work pieces are cleaned in the first stage, removed and subjected to two rinse stages, and then dried. It is important to monitor the concentration of cleaning agents which are dragged from the cleaning tank to the rinse tanks since the cleanliness of the work piece depends on the purity of the final rinse water.

Each type of cleaning agent may require a different type of wastewater treatment for the effluent generated. It is very important to investigate the types and amounts of materials that may be dissolved in the wastewater since some aqueous cleaning agents remove larger amounts of metals, e.g. lead, than CFC-113 or 1,1,1-trichloroethane.

Ultraviolet light/ozone cleaning

By applying large doses of ultraviolet light to the surface to be cleaned, ozone is created from the surrounding atmosphere. Ozone is a very reactive substance and oxidizes organic compounds to create carbon oxides and hydrogen oxides. These products are volatile and evaporate from the surface of the part being cleaned.

This type of cleaning technology is effective in removing organic residues from the surface of the part, but is ineffective on non-organic residue since the oxides formed are nonvolatile and remain on the surface of the part.

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REPLACEMENT OF OZONE-DEPLETING SUBSTANCES IN HONEYWELL SPACE AND AVIATION CONTROL PRODUCTS

I. INTRODUCTION

This case study focuses on the alternatives examined for implementation in Space and Aviation Control products. Honeywell Space and Aviation Control offers: systems integration capabilities, automatic flight control systems, electronic cockpit displays, flight management systems, precision components for strategic missiles, and other control technology for space and aviation applications. The combined usage of CFC-113 and 1,1,1-trichloroethane in 1988 for these facilities was approx. 590,000 kg.

II. PRINTED WIRING BOARD CLEANING

Space and Aviation Control assembles plated through-hole boards, mixed technology boards, and surface mount-only boards. The primary solvent used for cleaning in this application is Freon-TMS, an azeotrope of CFC-113 with methanol. The primary challenge for cleaning is in surface mount technology applications, which have tight clearances to the board and a high packing density of components on the board. A test board was designed with surface mount technology and a range of components from 50 mil to 20 mil pitch. Cleanliness was determined using surface insulation resistance testing, ionograph testing, and residual rosin testing. Material compatibility tests were also performed on the various materials found in the assembly of printed wiring boards.

Semi-aqueous solvents were selected as an interim step for the replacement of CFC-113 and 1,1,1-trichloroethane because of the high reliability and performance requirements of space and aviation products and because of the time-frame required for substitution. The implementation of semi-aqueous solvents required only a change in the cleaning material and no change of the flux since the semi-aqueous solvents were formulated to remove the traditional rosin residue. Six semi-aqueous solvents were tested and two were selected for implementation -- a terpene hydrocarbon and an aliphatic hydrocarbon. In-line and batch equipment purchased and installed in 1993 worked extremely well at the facilities. For example, a Minneapolis facility realized a US$400,000 savings in raw material costs in a single year because of the implementation of these alternative solvents. The semi-aqueous technology implemented also proved to be a viable alternative for high-reliability applications.

III. GYROSCOPES AND PRECISION GUIDANCE INSTRUMENTS

Momentum control gyroscopes and precision guidance instruments are used to control and detect movement in satellites, space probes and platforms, and missiles. Contamination-free surfaces are required during fabrication in order for these devices to operate reliably for extended periods of time in harsh military and space environments. The cleaning processes used must be compatible with a variety of materials, including: metals, thermoset polymers, thermoplastics, elastomers, lubricants, organic and inorganic coatings, and optical components. In addition, cleaning processes must be effective in removing contaminants such as hydrocarbon, ester, and fluorocarbon lubricants, handling debris, damping fluids, and process residuals.

For particle removal in critical cleaning operations, CO_2 "Snow", perfluorocarbon sprays, and water-based sprays were selected as alternatives to ozone-depleting solvents. Equipment has also been specially designed to use perfluorocarbon solvents for the removal of fluorocarbon oils and greases, while limiting solvent emissions to the atmosphere. Carbon dioxide is also being used in another cleaning process -- supercritical fluid cleaning -- for the removal of a wide variety of oils. Flammable and combustible solvents have also been employed for processes that are not compatible with other alternative cleaning solutions.

IV. CONCLUSIONS

The varied nature of the substrates being cleaned and the contaminants present, coupled with the required high reliability of military and space hardware, led to the development and implementation of a wide variety of cleaning processes and materials that use no ozone-depleting substances. Figure XI-1 shows the annual use of CFC-113 and 1,1,1-trichloroethane at the Honeywell Space and Aviation Control Operations. In 1988 the combined usage of these ozone-depleting solvents was 590,000 kg. By the end of 1993, the usage had decreased by 73% to 160,000 kg and the company saved millions of dollars in raw material costs. Many of the alternative processes implemented are new, while others like aqueous cleaning were already in use in cleaning applications but required further development and refinement for use on high-reliability hardware. The result of implementing alternative cleaning techniques for Honeywell Space and Aviation Control products was not less dependable equipment, but rather higher quality hardware whose cleaning processes have been thoroughly evaluated and qualified.

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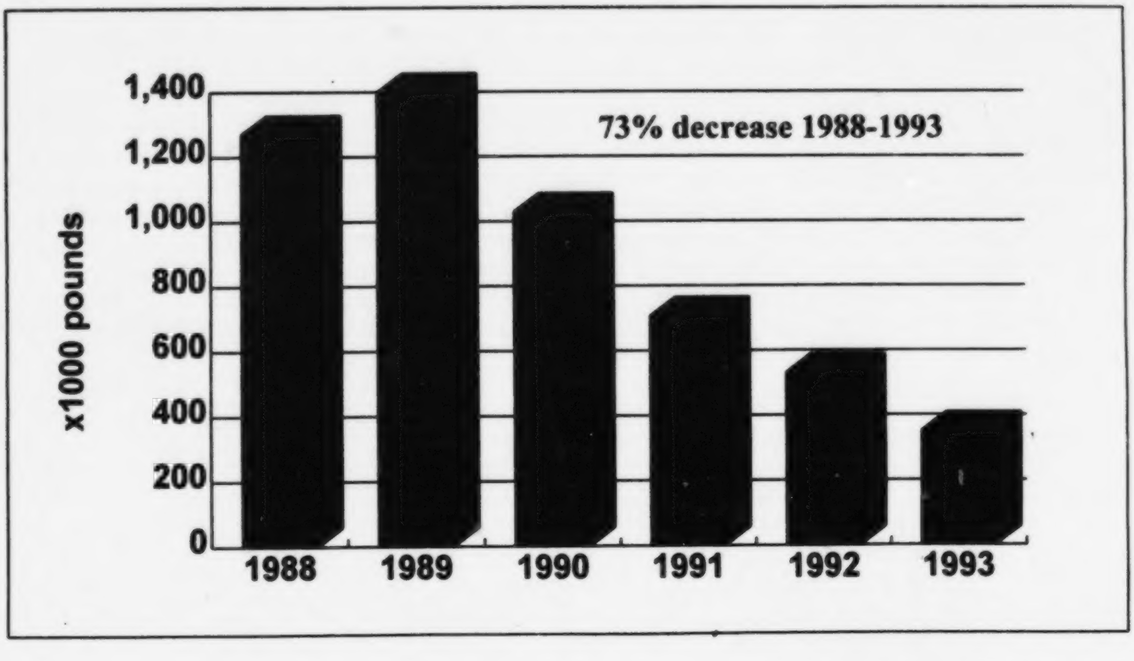
Figure XI-1

ANNUAL USE OF CFC-113 AND 1,1,1-TRICHLOROETHANE AT HONEYWELL SPACE AND AVIATION CONTROL OPERATIONS



ODS ELIMINATION AT IBM AUSTIN, TEXAS

I. SUMMARY

IBM was among the first companies to assess alternative cleaning technologies in order to take a proactive stance on the CFC Phaseout. After ruling out several options for its pilot project, the company successfully implemented aqueous cleaning. However, after no-clean technologies were further developed, the company adapted new, superior alternative.

II. INTRODUCTION

IBM Austin began a program to eliminate chlorofluorocarbons (CFCs) and 1,1,1-trichloroethane (TCA) from its manufacturing processes prior to the U.S. ratification of the Montreal Protocol. In 1987, IBM set goals to drastically reduce CFCs by 1991 and TCA by 1992. IBM finalized the company goals in 1990, setting the date for completion of CFC phaseout at 1993 and TCA phaseout at 1995.

IBM Austin concluded in 1987 that options that could be implemented immediately included HCFCs, semi-aqueous cleaning, and aqueous cleaning. HCFCs were viewed by IBM to be a short-term solution. No-clean technology was available but had been neither fully developed nor tested to meet IBM Austin's rigorous manufacturing requirements. Semi-aqueous technology, a new development at the time, required sophisticated fire protection systems to protect against flammability risks. Therefore, aqueous cleaning was chosen in 1987 as the best available solution to eliminate CFC and TCA usage. Aqueous cleaning would be only an interim solution until a no-clean technology that met IBM's manufacturing requirements was fully developed and qualified.

IBM Austin met its goals and completed the elimination of the use of CFCs during the first half of 1991 and the use of TCA by year-end 1992. Over one year after implementation of water-soluble materials, no-clean had become the least expensive of all non-ODS cleaning options, reinforcing IBM's original long-term goal to move to this technology.

The no-clean process reduces cost in several ways. First, it eliminates the cleaning stream as well as the waste stream. Other important cost-reducing elements are the elimination of floor space requirements for cleaning apparatus and the reduction in overall cycle time. With the elimination of cleaning operations, the number of required operators on the manufacturing floor can be reduced. The low cost of this option, in conjunction with recent progress made in developing advanced flux materials and the understanding of the remaining residues has made no-clean a viable alternative.

III. THE AQUEOUS CLEANING PROCESS

IBM examine several important elements in implementing the aqueous cleaning process. These included:

- equipment design;
- process parameter setup; and
- process control.

The cleaner selected was tailored to the needs of IBM's cleaning process and the type of flux selected. When specifying the materials of construction, IBM had to consider the flux activity and the corrosive nature of the residues.

Due to their low vaporization temperatures, typical solvents generally are dried with forced air only. Water, on the other hand, does not evaporate as easily and the design of the drying system for the aqueous cleaning system required a combination of forced air and heat. The introduction of high-velocity/high-volume blowers greatly improved the drying of many designs, but this method was not considered adequate for connectors with openings perpendicular to the air flow. Therefore, IBM selected a system with an optimal heating profile to ensure success.

Process parameter setup was critical to the successful implementation of aqueous systems. Therefore, in order to select an overall set of process parameters, IBM established a procedure was established to identify and evaluate the process interactions.

Process control was another key element in the implementation of aqueous cleaning processes. Process control is the ability to produce a product with consistent quality in mass production. Good controls ensure that the product is properly cleaned and that no corrosive residues are present that would have an adverse effect on the reliability of the final product. Methods for the measurement and control of the cleaning process included:

- equipment controls/statistical process control (SPC); and
- random temperature, humidity, and bias stress testing.

Random temperature, humidity and bias stress testing stimulates the durability and reliability of a product in the field.

IV. THE NO-CLEAN PROCESS

Implementation of no-clean technologies differed significantly from implementation of aqueous cleaning technologies. The elements of a program to implement no-clean materials included:

- probe testing/residue thickness;
- flux interactions/reliability;
- solderability on a copper surface;
- ease of manufacturing; and
- use of nitrogen as a controlled atmosphere.

Probe testing was the chief method used to detect assembly-process and electrical defects on printed circuit boards. Some no-clean fluxes leave non-corrosive residues on assemblies which inhibit this form of testing. In order to minimize this impact, no-clean methods had to be compatible with probe testing by leaving little to no residue on the probe surface.

Flux interaction with materials of construction was another critical factor. In all cases, whenever a new flux is to be implemented, compatibility with existing materials must be established. Although a rigorous chemical composition analysis also might have been effective, this was accomplished through reliability testing at IBM.

Initially, it was expected that solderability of the components and the carrier would pose a problem to the implementation of a no-clean process. It was thought that hot air solder level (HASL) cards would be required. Due to the added cost of solder levelling and the adverse effects on fine pitch processing, it was decided that any no-clean implementation would use bare copper boards with an organic protective coating.

The ease of manufacturing using solder pastes and fluxes was another prerequisite. IBM's minimum requirement for no-clean solder pastes was the ability to screen 0.41 mil pitch components. In fact, the robustness of the screen printing process was greatly improved as a result of switching to no-clean materials. Because flux chemistry turned out to be much more resistant to changes in the temperature and especially the humidity, resulting in better rheological performance.

Another important consideration during the implementation of no-clean processes was the use of inert gas. Nitrogen is used to control oxidation on bare copper surfaces, but its use added to the overall cost of soldering. The company's ultimate goal was to use nitrogen only over the wave solder pot, where dross reduction/elimination would provide an additional benefit.

Solder balls have long been considered a problem with the use of no-clean materials in that the solder balls are no longer removed during a subsequent cleaning process. The formation of solder balls attached to discrete chip components was a problem in one of IBM's processes. An analysis suggested that the pad size and dimensions contributed significantly to the problem. These problems where solved through a combination of design and processing controls.

From 1989 to 1993, IBM Austin eliminated the use of CFCs and TCA, and reduced water consumption through the implementation of no-clean technology processes:

- approx. 196,000 kg of CFC-113 phased out from peak 1988 usage
- approx. 140,000 kg of TCA phased out from peak 1988 usage
- Nearly 378.5 litres per minute water use eliminated.

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THE JAPAN INDUSTRIAL CONFERENCE ON CLEANING

I. SUMMARY

In response to the Montreal Protocol, the government of Japan enacted legislation phasing out the use of ozone-depleting substances, including the solvents 1,1,1-trichloroethane and CFC-113. However, users of these chemicals required assistance in implementing alternatives to these solvents because of the great diversity in applications, enterprises, and substitute chemicals and technologies. To provide this assistance, a new organization -- the Japan Industrial Conference on Cleaning (JICC) -- was formed. JICC will accomplish its mission through promoting mutual friendship and cooperation between members, disseminating and exchanging information, standardizing technologies, and providing a central point of contact with regulatory authorities.

II. INTRODUCTION

1,1,1-Trichloroethane and CFC-113 are scheduled to be phased out by the end of 1995 in developed countries. Total elimination of these substances entails developing and testing the most appropriate alternative chemicals or technologies for each application. To accomplish this task, each of the issues listed below must be considered:

1. Diversity of application

   Solvent applications are diversified, involving cleaning many different types of contaminants from a wide variety of parts. In addition, some applications involve additional processes before and after cleaning. Hence, the individual requirements of each process must be considered in order to select the most appropriate alternative.

2. Diversity of enterprises

   Many different sizes of manufacturers have been using ozone-depleting solvents, with medium and small enterprises accounting for more than 50 percent of total consumption in Japan. As a result of these circumstances, it is important to ensure good contact between users of solvents and manufacturers of alternative technologies.

3. Diversity of alternatives and substitutes

   An investigation of the wide array of alternatives and related technologies is essential to selecting the best option for each application. In addition, users should conduct comprehensive testing to ensure the success of the new chemical or technology.

III. ESTABLISHMENT OF A NEW INDUSTRIAL ORGANIZATION

The Japan Industrial Conference on Cleaning was established in April 13, 1994 to assist in phasing out ODS solvents. Members of JICC are enterprises involved in supplying equipment and chemicals for various cleaning technologies, including ultrasonic cleaning, spray cleaning, vacuum cleaning, and high-pressure cleaning.

IV. JICC OBJECTIVES

JICC furthers the development of non-ODS cleaning technologies, contribute to environmental protection, and promote the expansion of business in related fields by working toward a number of objectives.

Mutual friendship and information exchange between members, especially in different industrial fields. JICC aims to aid in the exchange of information to support business activities not only for suppliers of cleaning technologies, but also for users of such technologies.

Dissemination of information on cleaning technologies through educational materials and outreach efforts. JICC facilitates the understanding of new cleaning technologies. Educational materials will stress a "total system" approach, focusing on the strong interdependencies between each segment of industrial processes and the cleaning process.

Mutual cooperation to further the development of new technologies. In particular, JICC will increase and enhance cooperation between different fields of technologies.

Standardization of related technologies in order to ease the decision process faced by owners of existing cleaning equipment. Equipment owners are now faced with a wide array of options in considering their conversion to alternative technologies and are in need of some way to reduce their selections to the best technology for their application. To meet each user's requirements, JICC intends to investigate which features can be standardized on each technology, such as safety and environmental protection features to meet legal requirements.

Contact with administrative authorities to deal with special issues which would be difficult to handle by independent associations. JICC will be become industry's central point of contact with administrative authorities in the government and to effectively voice industry's concerns in preparation for legislation on present and future global environmental issues.

V. JICC MEMBERS

JICC is comprised of four types of members. Regular members are enterprises which manufacture cleaning equipment, cleaning agents, and auxiliary equipment. Supporting members are enterprises that support JICC's activities and assist in achieving JICC's objectives. Group members are groups that support JICC's activities and assist in achieving JICC's objectives. Finally, special members are groups that support JICC's activities and assist in achieving JICC's objectives and are also endorsed by JICC's board of directors.

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THE ELIMINATION OF 1,1,1-TRICHLOROETHANE IN ELECTRONICS CLEANING AT LOCKHEED SANDERS COMPANY

I. INTRODUCTION

An important part of the manufacturing process for printed circuit boards and other electronic components is the removal of residues during the post-assembly cleaning process. In recent years, the Lockheed Sanders Company used 1,1,1-trichloroethane (TCA) for cleaning electronic components. However, in an effort to protect the environment and reduce operating costs, Sanders is eliminating the use of TCA from its cleaning operations. This effort has been implemented through a Sanders Process Action Team.

II. PROCESS DESCRIPTION

The two standard processes for electronic component cleaning at Sanders were vapour degreasing and immersion cleaning with TCA. Due to concern for ozone layer protection and rising costs associated with TCA-based cleaning as the production phaseout date approaches, Sanders tested several alternative cleaning processes. Sanders chose two spray cleaning systems to replace TCA for cleaning in surface mount technology (SMT) applications.

Stencil Cleaning

Sanders selected the EMC Global Technologies Model IPA-30 batch cleaner for stencil cleaning. The batch cleaner is a closed-loop, explosion proof machine incorporating a wash and a dry cycle. Figure XI-2 shows a simplified version of the stencil cleaning process. Isopropyl alcohol (IPA) is sprayed onto circuit boards via rotating spray arms at high-volume and low-pressure during the wash cycle. Excess alcohol evaporates in the dry cycle when air is pumped through the rotating arms.

Printed Circuit Board (PCB)

A Hollis/Electrovert HS-332 cleaning machine with Alpha 3555 saponifier is now used to clean assembled SMT circuit cards. The cleaning solution is a concentrated alkaline liquid designed to remove flux residues from soldered electronic assemblies. Its characteristic low foaming and high surface insulation resistance (SIR) satisfy the performance requirements of the cleaning process. Figure XI-3 details the cleaning process flow for the circuit card cleaning system. In the wash cycle the cleaning solution is heated and sprayed onto the circuit cards with high volume, high pressure jet nozzles. A recirculating pump returns the solution to a holding reservoir for reuse. Once the PCBs have been washed with the cleaning solution they are spray rinsed with deionized water to remove excess cleaner and residues. The parts are dried using "air knives" to remove all moisture that may be trapped in crevices and are passed through a convection heating station to ensure that all parts are completely dry. Finally, the cleaning solution is transferred to an external ultrafiltration unit where it is recycled and stored for the next cleaning cycle. However, due to the build up of dissolved metals and gradual degradation of the saponifier over time, the cleaning solution must be changed periodically. Rinsewaters are being treated using activated carbon and ion exchange resin beds to form a "closed-loop" rinsewater system.

Figure XI-2

LOCKHEED SANDERS COMPANY STENCIL CLEANING PROCESS

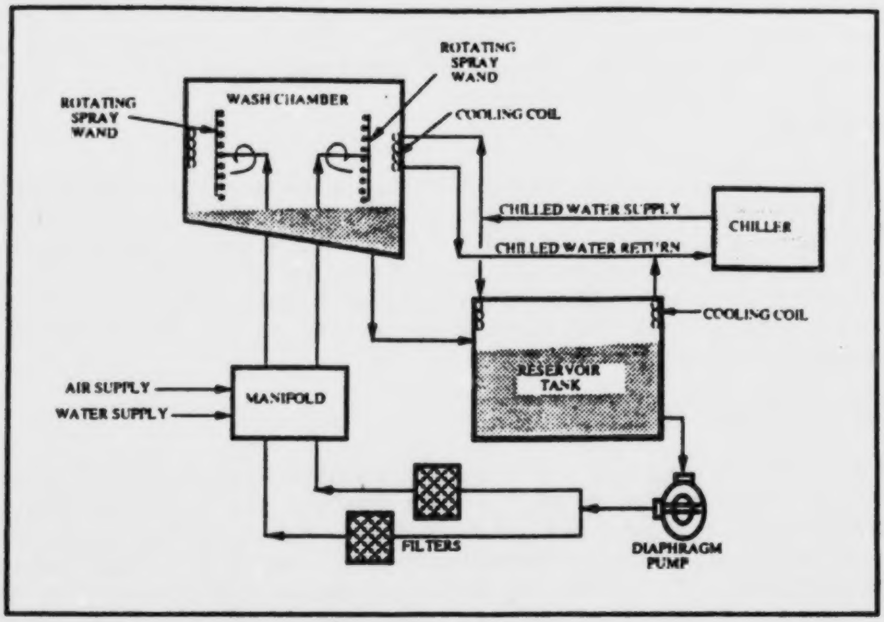
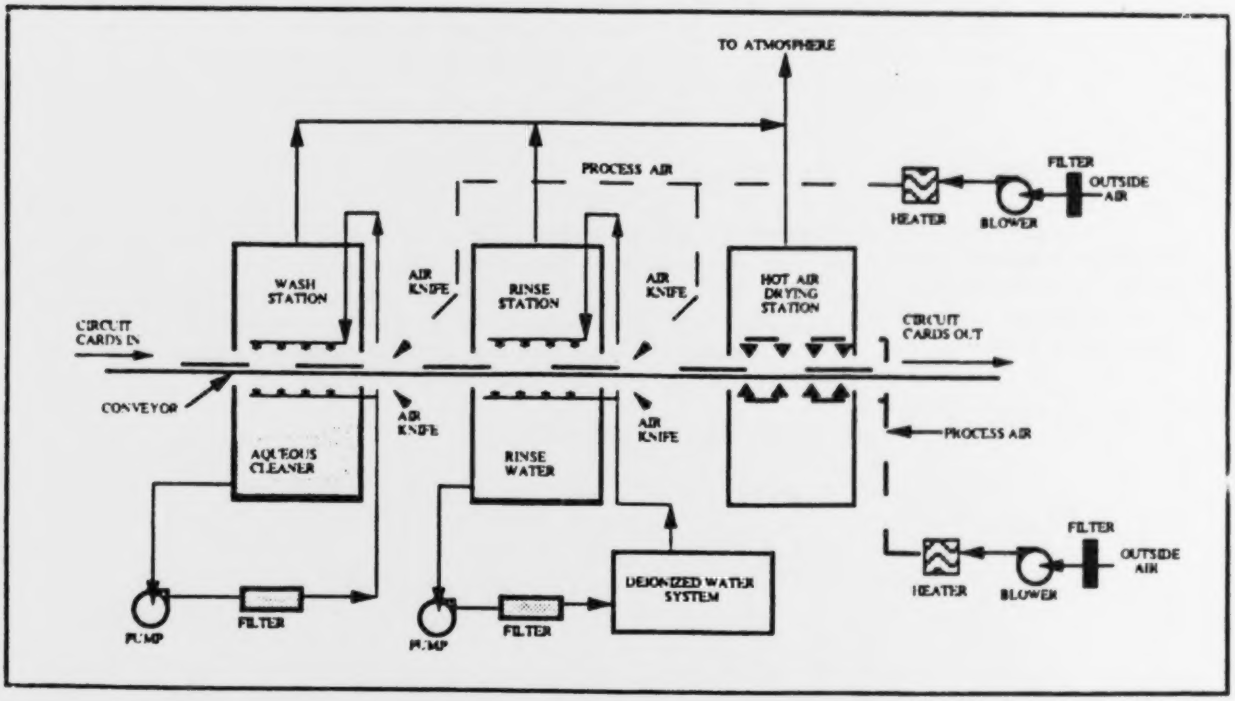

ROTATING SPRAY WAND
WASH CHAMBER
ROTATING SPRAY WAND
COOLING COIL
CHILLED WATER SUPPLY
CHILLER
CHILLED WATER RETURN
COOLING COIL
RESERVOIR TANK
AIR SUPPLY
WATER SUPPLY
MANIFOLD
FILTERS
DIAPHRAGM PUMP

Figure XI-3

LOCKHEED SANDERS COMPANY CIRCUIT CARD CLEANING PROCESS


TO ATMOSPHERE
PROCESS AIR
FILTER
OUTSIDE AIR
HEATER
BLOWER
WASH STATION
AIR KNIFE
RINSE STATION
AIR KNIFE
HOT AIR DRYING STATION
CIRCUIT CARDS IN
CIRCUIT CARDS OUT
CONVEYOR
AIR KNIFE
AIR KNIFE
AQUEOUS CLEANER
RINSE WATER
PROCESS AIR
FILTER
OUTSIDE AIR
HEATER
BLOWER
DEIONIZED WATER SYSTEM
PUMP
FILTER
PUMP
FILTER

III. BENEFITS & LIMITATIONS

Some of the benefits of using both aqueous and IPA cleaning processes in place of TCA cleaning include:

- elimination of the use of ozone-depleting chemicals
- effective removal of ionic compounds
- components cleaned maintain high surface insulation resistance (SIR)
- enclosed equipment reduces vapours in the workplace
- lower operating costs

Limitations of the aqueous and IPA cleaning processes include:

- IPA is flammable and must be used with extreme care
- Alpha 3555 is combustible and corrosive
- Alpha 3555 is comprised of several constituents with low Threshold Limit Values (TLVs) (two constituents each accounting for 40% of the formulation have TLVs of 3 ppm and 50 ppm)
- space required for alternative cleaning systems is typically larger than for the TCA system

IV. PLANNED PROCESS IMPROVEMENTS

Lockheed Sanders Company is also evaluating a water soluble flux to further enhance the soldering process and minimize waste generation. The flux under consideration, Alpha WS-360, is a halide-free organic flux which leaves a negligible amount of residue after the soldering process. Implementation of the water soluble flux would eliminate the use of IPA in stencil cleaning.

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HYDROCARBON DRY CLEANING AT MILJOMINISTERIET

I. INTRODUCTION

The Center Rens in Helsinge, Denmark has demonstrated that Satec's reloading hydrocarbon dry cleaning system can replace CFC-113 as a dry cleaning solvent for cleaning fabrics and leather. It has also been determined that a large portion of perchloroethylene cleaning can be replaced with hydrocarbon cleaning.

II. PROCESS CHARACTERISTICS

The higher initial cost of the Satec hydrocarbon dry cleaning system is a significant factor discouraging Danish dry cleaners from investing in the new equipment. However, the price of a comparable perchloroethylene machine is expected to increase as future European Community regulations restrict the use of chlorinated solvents. At Center Rens, the operating costs for hydrocarbon cleaning systems are the same as for CFC-cleaning systems. Hydrocarbon cleaning may also be less expensive for dry cleaning establishments situated in municipalities which impose high taxes for waste disposal.

With the implementation of the hydrocarbon dry cleaning process, cleaning solvent consumption was reduced by approximately 60 percent. The use of hydrocarbons is estimated to be slightly more than one percent per kg of clothes cleaned. Other significant characteristics of the hydrocarbon technology include:

- The consumption of energy which might be increased with hydrocarbon cleaning, however, energy use has not been compared.
- Water consumption is independent of the technology because cooling water is recirculated.
- The emission of ozone depleting substances will end.
- There will be an increase in the emissions of hydrocarbons which contribute to the formation of "smog".
- Waste quantity (distillation residue, sludge of textile fibres, fluid-containing filters) will remain unchanged, but the character of the waste will be changed to flammable oil waste, which is more economic to dispose.
- Wastewater consists of water with a very low hydrocarbon content (< 20 ppm). Cooling units without water recovery also produce some wastewater (80 litres per charge).
- Hydrocarbon vapours in the dry cleaning room appear in low concentrations (< 5% of the threshold limit value).
- Air change requirements will vary between 3 and 10 times per hour most of the year, because of the need to keep the shop doors open to allow heat from the process to escape.
- Risk to unprotected skin is considered low, but the use of protective gloves is highly recommended.
- The Danish EPA does not consider that flammability is a major risk. However, it is recommended that normal precautions for handling flammable substances be taken.

III. CONCLUSIONS

The Danish EPA supported the Hydrocarbon Dry Cleaning project where hydrocarbons replaced CFC-113 and perchloroethylene in dry cleaning operations. The project was carried out successfully without increasing risk for the workers in the facility.

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PHASING OUT OF OZONE-DEPLETING SUBSTANCES BY THE MINEBEA CO. THROUGH THE USE OF A WATER-BASED CLEANING SYSTEM

I. INTRODUCTION

The Minebea Co. in Thailand and Japan has developed and implemented a water-based cleaning system to clean miniature ball bearings and other parts. The water-based cleaning system eliminates the use of ozone-depleting substances such as CFC-113 and 1,1,1-trichloroethane. The cleaning system utilizes ultrasound and deoxidized water and reduces the load on wastewater treatment systems by eliminating the need for anticorrosive agents in the rinsing process.

II. OPERATION OF THE WATER-BASED SYSTEM

The water-based cleaning system operates through the use of ultrasonic energy and deionized water. Ultrasonic energy in water causes the pitting or wearing away of debris from metal surfaces (a process known as cavitation). Use of deoxidized water in this cleaning process acts both to enhance cavitation, and thus cleaning, and curbs rusting of steel surfaces because the rate of rusting is proportional to the concentration of dissolved oxygen in the water.

Figure XI-4 is a diagram of a water-based cleaning system. The parts enter the detergent bath, followed by the rinse bath where deoxidized water is added, and continue on to the dryer. The water from the rinse bath is sent to the waste water treatment system.

III. CONCLUSIONS

The water-based cleaning system which uses deoxidized water provides several advantages over other cleaning methods. Deoxidized water enhances the effect of ultrasonic energy in washing and curbs rusting of steel. In addition, the use of a deoxidized system eliminates the need for anticorrosive agents in rinsing and thereby reduces the load on wastewater treatment systems.

The Minebea Co. believes that a water-based washing system must be designed to realize maximum washing effect with minimum water consumption.

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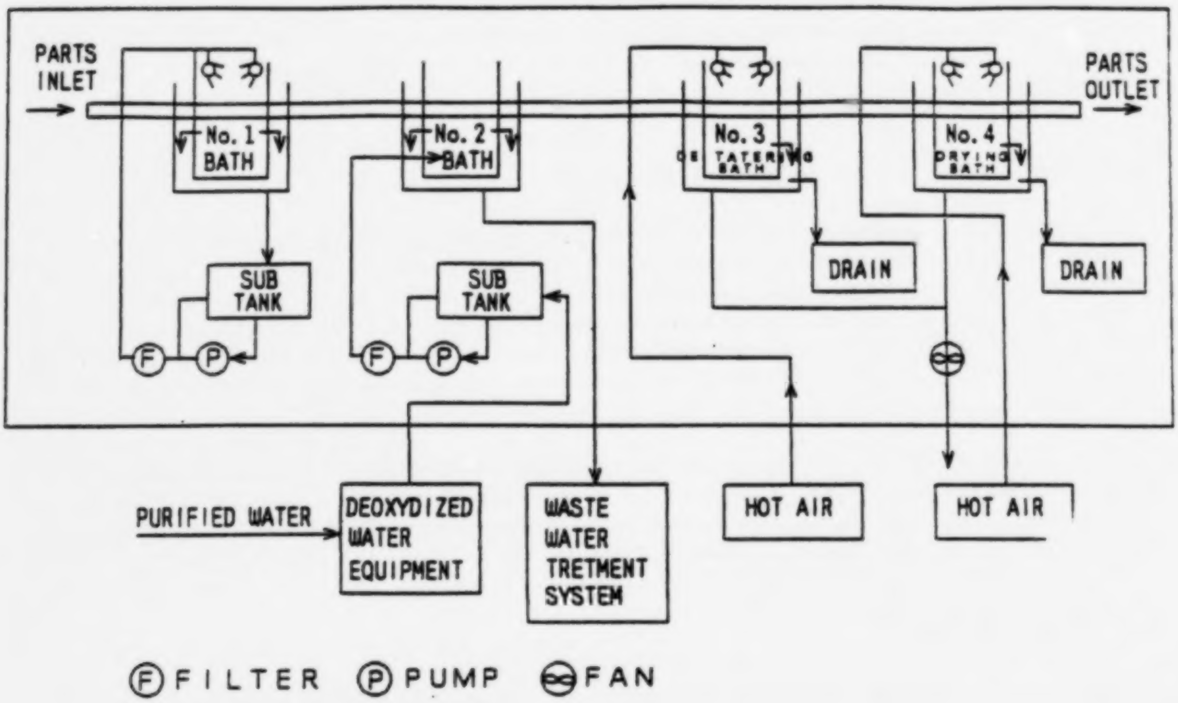
Figure XI-4

MINEBEA COMPANY'S WATER-BASED CLEANING SYSTEM


PARTS INLET
PARTS OUTLET
No. 1 BATH
No. 2 BATH
No. 3 DEWATERING BATH
No. 4 DRYING BATH
SUB TANK
SUB TANK
F
P
F
P
DRAIN
DRAIN
PURIFIED WATER
DEOXYDIZED WATER EQUIPMENT
WASTE WATER TRETMENT SYSTEM
HOT AIR
HOT AIR
F FILTER
P PUMP
FAN

bath no.	solvent	others
1	detergent	filtering
2	purified and deoxydized water	filtering
3		hot air
4		hot air

NON-ODS ALTERNATIVES IN THE CLEANING OF INTEGRATED CIRCUITS AT NATIONAL SEMICONDUCTOR - MALAYSIA

I. INTRODUCTION

As part of a partnership between the Malaysian Government and industry to eliminate the use of ozone-depleting solvents in cleaning operations, National Semiconductor in Penang, Malaysia worked closely with the government on efforts to find alternatives to the use of ODS in industry. This effort lead National Semiconductor to implement changes in its cleaning operations for Integrated Circuits (ICs).

II. SELECTION OF AN ALTERNATIVE PROCESS

The ODS elimination efforts at National Semiconductor were a result of active employee involvement in environmental programs, lead by company management. The environmental efforts were coordinated by a Task Force leader. The Task Force was comprised of representatives from a number of the company's divisions, including, Process Engineering, Plant Engineering, Maintenance, Material Control, and Purchasing.

The criteria for selecting ODS alternatives included:

- quality and reliability of the finished products
- workplace health and safety, and environmental impact,
- capital investment/Return on Investment (ROI)
- Ozone Depletion Potential (ODP)/Global Warming Potential (GWP)
- process flexibility, including transition to new equipment, and worker training.

III. PROCESS IMPLEMENTATION

In the implementation stage an alternative cleaning process was identified based on the criteria described above. In the new "Green" process, pre-solder M-Pyrol cleaning step was replaced with a citric acid wash. In addition, wave soldering was replaced with solder plating in the new process. The ODS cleaning in the old process was replaced with a hot deionized (DI) water rinse, and ambient air drying was replaced with hot air drying.

Overall, the "Green" process resulted in an increase in output from 18,300 units/hour to 84,500 units/hour. The new process resulted in very consistent product quality, while reducing the chemical cost per unit to 1/3 of the original cost. In addition, the new process equipment was easy to clean and maintain while the original equipment required significant effort to clean.

IV. CONCLUSIONS

Implementing the new cleaning system required a total capital expenditure of $250,000 as well as special training for workers on the new equipment. The new cleaning system not only resulted in improved cleaning at

National Semiconductor, but was also a positive step towards the elimination of ODS use in all industry in Malaysia.

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IMPLEMENTATION OF ODS ALTERNATIVES AT NAVAL AVIATION DEPOT CHERRY POINT

I. SUMMARY

The Naval Aviation Depot (NADEP) at Cherry Point, North Carolina is responsible for a variety of aircraft maintenance activities that originally required extensive use of ozone-depleting solvents. Since that time, cabinet-style aqueous parts washers, aqueous ultrasonic processing, and non-ODS methods of cleaning parts by hand have all been significant steps towards NADEP's goal of eliminating ODS use. While phaseout efforts have depended upon equipment procurement and technology development, the attitudes of the work force and cooperation between departments within the facility have been the most important factors in the success of the program.

II. INTRODUCTION

NADEP performs repair, overhaul, maintenance and engineering support functions on a variety of weapons systems including the C-130 aircraft, the H-46 helicopter, the AV-8B vertical/short take-off and landing (V/STOL), and the V-22 tilt-rotor aircraft.

Repair and maintenance requirements frequently required the use of a wide variety of hazardous or environmentally harmful materials, including ODSs. Cleaning prior to inspection, repair, testing or reassembly all relied on the performance of these types of materials. The primary substances used in these cleaning tasks until 1990 were 1,1,1-trichloroethane and CFC-113.

Large-batch vapour degreasing with 1,1,1-trichloroethane was the preferred method of cleaning aircraft and engine components. Fourteen degreasers were in use in 1990 and accounted for the bulk of ODS usage in the facility. The two degreasers located in the engine cleaning shop and plating facility alone consumed 75 percent of the 1,1,1-trichloroethane used in 1990.

Cleaning parts by hand in bench-top applications was another activity requiring large amounts of ODSs.

NADEP identified the largest factor affecting its overall consumption of ODSs as being the non-critical use of ODSs in solvent cleaning. Seventy five percent of total ODS consumption was for applications for which alternatives were already available at the depot. For this reason, NADEP decided that its goal should be ODS elimination, not just reduction.

III. INITIATING CHANGE

Once NADEP had finished its survey of ODS consumption in its maintenance procedures, it developed an action plan. The plan initially focused on training the entire workforce that NADEP's goal was to eliminate ODS use. First, all of the product support engineers were briefed on their new responsibilities -- to stop specifying ODSs in new engineering directives and to review existing directives to identify ODS requirements. Production artisans also had to be aware of the new mission since personnel in the production shops had to be strong allies during this process. Depot management also took the initiative to include pollution prevention briefings during regularly scheduled shop safety meetings, focusing the discussion on specific materials and processes within that shop that would be affected by the ODS elimination.

Engineering personnel targeted the largest critical use for its initial ODS elimination efforts -- the vapour degreasers in the plating facility and in the cleaning shop. They required that engineering and shop personnel accept responsibility to ensure maximum results from any expended efforts. Engineering personnel first had to identify all uses of the vapour degreasers, and then investigate and approve alternative cleaning processes. They also had to be available during the implementation phase to troubleshoot any problems that arose. Shop personnel had to be willing to try new products or procedures and also had to be committed to working with engineering personnel to develop alternative processes.

Management also recognized that while engineering and shop personnel carried responsibility for process changes, individuals from throughout the facility would need to lend support in order to successfully implement change. A depot-wide effort was undertaken involving personnel in facilities and equipment engineering, capital procurement and budgeting, environmental engineering, safety, and maintenance.

IV. EXAMINING ALTERNATIVES

The first alternative investigated to replace vapour degreasing was aqueous immersion using alkaline detergent. A variety of cleaning products were tested using various temperatures, exposure times, parts orientation, and agitation methods. After completion of testing, NADEP concluded that this option would not satisfactorily replace vapour degreasing for its applications.

The second alternative investigated was a cabinet-style parts washer. The unit applied a hot solution of aqueous detergent at pressures from 40 to 220 psi. After the initial engineering evaluation, production personnel visited the manufacturer of the parts washer to evaluate cleaning performance on actual parts. After they witnessed the performance of the parts washer, they became convinced that this technology would perform adequately for their needs and subsequently procured three units for initial implementation.

However, NADEP found during implementation that the parts washers were not effective on all types of soil, and thus did not totally eliminate the need for the vapour degreasers. Other technologies were investigated and NADEP found that for the removal of carbon, wet sodium bicarbonate blast units were more effective than the parts washers. Both open-blast and glovebox wet-type units were procured for this application.

Since the technologies had been so successful at supplanting the vapour degreasers, a date was set to "lock-out" the vapour degreasers in these shops. Engineering and shop personnel then worked to have the alternate processes operational in time to meet this goal.

During commissioning of the parts washers, NADEP found that, while shop personnel were pleased with the performance of the washers, it was difficult to handle the existing work load without improving the design of the loading baskets. Through trial and error, facility personnel developed round, covered, compartmentalized baskets that greatly improved the shop's satisfaction with the production of the new process.

While struggling to eliminate the largest uses of 1,1,1-trichloroethane, NADEP was also evaluating the largest uses of CFC-113. The electric motor shop was using a large CFC-113 ultrasonic unit that consumed 6,800 kilograms per year in a relatively inefficient manner. A new ultrasonic unit, suitable for use with aqueous cleaning solutions was implemented, which performs equally well.

To continue its evaluation, NADEP tried cleaning parts previously cleaned ultrasonically with CFC-113, in one of the new cabinet style parts washers. Test results indicated that these parts were cleaned just as thoroughly by the new aqueous parts washer but with significantly higher throughput. The change resulted in a significant reduction in turnaround time for the parts originally cleaned with CFC-113.

V. ALTERNATIVES FOR HAND CLEANING

Non-ODS substitutes for cleaning parts by hand have proven more difficult to locate than substitutes for batch processes because of NADEP's many requirements of solvents used in this application. These requirements include:

- good performance at room temperature;
- good performance without rinsing;
- a flashpoint above 140° F; and
- the solvent cannot contain any products from the EPA's list of 17 high-priority toxic substances.

NADEP found some petroleum/terpene products and aqueous products meeting MIL-C-85570 Type II to be suitable for many applications. However, these two types of materials did not satisfy the requirements of all the depot's clean-by-hand applications, especially some precision cleaning tasks. Processes and materials are still being evaluated for these applications.

NADEP's current philosophy for clean-by-hand applications has been summarized on videotape and is being used as a training supplement. The depot's philosophy dictates the use of batch cleaning methods whenever possible, with use of the least objectionable chemicals when cleaning by hand.

VI. REMAINING ODS REQUIREMENTS

Oxygen system cleaning has proven to be the most difficult challenge for ODS elimination. NADEP is working together with the Naval Sea Systems Command and others within the Naval Air Systems Team, in the evaluation of alternative materials and processes for this application. NADEP is optimistic that alternatives will be identified by the end of 1994. At the request of the

North Atlantic Treaty Organization (NATO), the U.S. Air Force and the U.S. EPA are organizing a global effort to solve these problems.

VII. SUMMARY

The ODS elimination effort at NADEP has been largely successful because of the dedication of personnel throughout the facility toward meeting this common goal. The benefits have also been shared by the entire workforce through reduced costs, reduced turnaround time, and pride in protecting health, safety and the environment.

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CFC-113 ELIMINATION AT NORTHERN TELECOM

I. INTRODUCTION

Over a period of three years beginning in 1988, Northern Telecom invested approximately $1 million in a CFC-113 phaseout program. The immediate payoff from this investment was $4 million. The savings came first from conservation measures that reduced purchases of CFC-113 cleaning solvents, and ultimately from the implementation of an innovative "no clean" technology that eliminated the need for cleaning altogether.

When the project started, Northern Telecom was using 1,000 tons of CFC-113 each year. The corporation succeeded in eliminating CFC-113 use from its manufacturing operations worldwide in 1992, which at that time was nine years ahead of the date set by the Montreal Protocol (The Protocol has since been revised.).

The business case for CFC elimination was not the initial impetus for the project, but instead emerged gradually as the project progressed. The decision to undertake such an aggressive environmental challenge to the corporation came from a group of seventy Northern Telecom engineers, who came together at an internal CFC Workshop in 1988 to consider the impact of the Montreal Protocol on the corporation's activities.

At the time, Northern Telecom, like other manufacturers in the industry, relied heavily on the use of CFC-113 to remove flux residue from printed circuit boards. CFC-113 was considered the most effective cleaner available and was relatively safe to use, with low toxicity and flammability levels. The challenge was to find a safe alternative that would satisfy customer requirements for high-quality, reliable products at an affordable price.

II. THE PHASEOUT PROCESS

The CFC Workshop set the ambitious goal of meeting this challenge within three years, and a Task Force was set up to accomplish this goal. Management commitment to the project, both from the corporate environment function and from the operational side, played an important role in the project's eventual success. The Task Force had access to the most senior levels of management in the corporation, as well as close working relationships with contacts in each of Northern Telecom's forty-two manufacturing plants.

In order to "fast-track" the process, the Task Force was organized into three teams, each of which took on a different assignment. One team was responsible for finding ways to reduce CFC consumption through conservation. Initial results from one test location were impressive, and technological changes had succeeded in controlling loss and unnecessary evaporation of the solvent into the atmosphere. An improved CFC-113 distribution system included a software package, designed by Northern Telecom engineers, that monitored and managed metering devices and leak detectors connected to the piping system. Within months, CFC-113 requirements had been reduced by 50 percent. The addition of activated charcoal absorption reduced the needs still further. It was estimated that the savings from the decrease in CFC-113 purchases would pay for the new technology in under two years.

A second team was responsible for finding effective and safe cleaning alternatives. A number of options were considered, including water and alcohol cleaning processes, and alternative solvents such as terpenes. The feasibility assessment for each option took into account a number of variables including: process compatibility, flexibility and performance, capital costs, operating costs, and safety and environmental issues. In order to assess the technical feasibility of each option, the team developed a "difficulty index" that compared the degree of difficulty of using a non-CFC process with that of the CFC-113 process. The economic feasibility was evaluated using the net present value of the two processes.

The interest of this group was soon caught by the possibility of eliminating the need for cleaning altogether. The long-term solution selected by the team was the "no clean" process, which involves the controlled application of a low-solids flux containing only alcohol and 1-3 percent solids. If properly managed, the residue remaining on the boards after the soldering process does not detract from product reliability. A board duster can test the cleanliness of the circuit board by applying a fine spray of powder to the surface of the board and measuring weight gain. When no weight gain occurs, the board has met the cleanliness standards.

The crucial factor in implementing the "no-clean" process was ensuring that customers had confidence in the new process. The third Task Force team had been interacting with outside stakeholders in the project. They had been sharing project progress with governments, media, customers, suppliers, environmental groups, and the general public. Northern Telecom manufacturing plants had been working closely with suppliers who were developing new chemical formulations and fluxes. In one project, Northern Telecom engineers collaborated with chemical producers, flux and equipment manufacturers, government agencies, industry associations, and the U.S. military on a project to set cleanliness standards for circuit boards used by the military. Customers were involved in shaping and monitoring the testing of the new technology, and found that the resulting circuit boards were as clean as those manufactured using CFC-113 cleaning. In fact, improvements in quality had actually been obtained.

By December 1991, all of the locations originally involved in the project had met the company's CFC-113 elimination target. Eight of the fifteen new plants involved due to Northern Telecom's 1991 acquisition of STC Plc in the United Kingdom had also become CFC-113 free. The other seven had committed to eliminating CFC-113 use by early 1992, complying with Northern Telecom's policy that any new acquisitions would have up to fifteen months to meet the corporate standard.

III. TECHNOLOGY COOPERATION

Cooperation with outside groups had been a key element in the Northern Telecom project's success. In 1989, Northern Telecom joined with one of its competitors, AT&T, and with the U.S. Environmental Protection Agency (U.S.EPA) to form the Industry Cooperation for Ozone Layer Protection (ICOLP -- now known as the International Cooperative for Ozone Layer Protection). ICOLP's continuing mandate is to promote the worldwide exchange of non-proprietary information on ozone-depleting solvent alternatives. It now has 12 multinational member companies, and has, as affiliated members, research and development institutes, environment ministries, military, and non-governmental organizations from Canada, China, France, Japan, Korea, Mexico, Russia, Sweden, Taiwan, Turkey, United Kingdom and United States.

ICOLP members provide experts to participate in conferences and workshops, write technical manuals, undertake special projects, and participate in technology cooperation projects. One of Northern Telecom's contributions to ICOLP was the creation of OZONET, an electronic information system on ozone-depleting solvent alternatives. The database, now part of the United Nations Environmental Programme OzonAction database, is available via modem from many parts of the world.

Under the auspices of ICOLP, Northern Telecom participated in a 1991 technology cooperation project, working in partnership with the Government of Mexico, the Mexican association of industries, and the U.S. EPA. The project was designed to help the Mexican electronics industry eliminate the use of ozone-depleting substances through workshops and on-site technical assistance. The collective efforts of the partners in the program have achieved substantial success -- a 70 percent reduction in ozone-depleting solvent use in Mexico. The program has also introduced Mexican manufacturers to the latest and best alternative technologies, thereby improving their competitive advantage in the global economy.

In 1993, the World Bank agreed to provide ICOLP with money from the Multilateral Fund set up under the Montreal Protocol, to help ICOLP launch a "global solvents" project. This money has paid for part of the cost of technology cooperation initiatives that have since been launched in seven countries. On each project, one or more ICOLP companies have taken the lead in managing activities in cooperation with a designated host country agency. Motorola led an initiative in Malaysia, and IBM took the lead in Korea and Taiwan. Other ICOLP companies have partnered with the Japan Electric Manufacturing Association and the Japanese Ministry of International Trade and Industry to lead a cooperative effort with industry and the government of Thailand. This year, the Ministry of the Electronics Industry in China agreed to work in partnership with Northern Telecom on a program to help the chinese electronics industry eliminate the use of ozone-depleting substances. Northern Telecom served as project manager for an initiative in Turkey, will lead workshops in India, and is starting to plan projects in Brazil and Vietnam.

Northern Telecom's leadership in CFC-113 elimination and its willingness to share its experience have brought it international recognition, including three prestigious awards: the U.S. Environmental Protection Agency's Stratospheric Ozone Protection Award, the United Nations Environment Programme's North American Leadership Award, and the U.S. President's Environmental and Conservation Challenge Award for Innovation.

IV. CONCLUSION

While the environmental challenge set by the Montreal Protocol was the spark for this ambitious project, Northern Telecom has seen direct business benefits. These include direct cash savings, a heightened international reputation for environmental leadership, and improved relationships with customers, suppliers, government agencies and other stakeholders. This experience has created an atmosphere of management support for environmental projects, and opened the door for new initiatives in such areas as product life cycle management and environmental management systems.

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REPLACING SOLVENT CLEANING WITH AQUEOUS CLEANING AT ROBERT BOSCH CORPORATION

I. SUMMARY

Robert Bosch Corporation's Charleston, South Carolina plant has been successful in replacing ODS cleaning solvents with non-chlorinated solvents. The technologies implemented have all cleaned as well or better than the original chlorinated solvents and have done so with reduced capital costs and similar or reduced labour costs. This result is due in part to the fact that ODS usage has been eliminated at a time when ODS prices have more than tripled. In addition, by using this opportunity to implement more energy efficient technologies in the phaseout process, the electric costs for its cleaning processes have been cut in half. Bosch is convinced that the time and resources already spent in converting from chlorinated solvents have been a good investment, and the company will continue to pursue these activities until all trichloroethylene (TCE) and hydrocarbon solvents have been replaced.

To date, Bosch has eliminated all CFC-113 usage and two thirds of its trichloroethylene (TCE) usage. The company's goal is to be completely free of chlorinated solvent usage by the end of 1995. These changes in cleaning processes have not only responded to the environmental goals of the Montreal Protocol and EPA's 33/50 Program, but have also resulted in improved cleaning at significantly reduced costs.

II. INTRODUCTION

The Robert Bosch Corporation is a U.S. subsidiary of Robert Bosch GmbH of Stuttgart, Germany. Bosch's Charleston plant manufactures automotive products and is the largest plant in the U.S. subsidiary, with about 1,700 people working in 600,000 square feet of manufacturing space. The plant has a heavy engineering emphasis in support of its assembly and test functions.

The primary products produced in the plant are gasoline fuel injectors, anti-lock brake systems, and diesel fuel pumps. The metal parts manufactured in the plant were cleaned with CFC-113 and TCE. The company plans to eliminate the use of TCE in support of the EPA's 33/50 Program and in response to the availability of improved cleaning efficiency and product performance associated with new replacement cleaning technologies. Eliminating chlorinated solvents on the production floor required a large team effort. Team participants included the plant manager, planners and users of the solvent replacements, and other support personnel.

The implementation of non-chlorinated solvents began in early 1990. By the end of 1992, all CFC-113 use had been eliminated by adopting alternative technologies. These processes are continually being reevaluated and improved; certain types of replacement processes described have been superseded by newer measures, and additional upgrades will continue to be introduced.

A key decision made early in the process was to replace the Company's large aging central degreasing stations with a number of small cleaning units, each designed and dedicated for cleaning just one type of part at one step in the product assembly process. This strategy required reassessment of each cleaning step and the identification of equipment and chemistry for optimizing each aqueous replacement.

As a result of this decision, annual use of approx. 247,000 kg of CFC-113 use has been eliminated at the Charleston plant, along with the approx. 41,000 kg of TCE. In addition, major cost savings have been realized by implementing more energy efficient aqueous cleaning technologies. The Company's records indicate that the combined costs of chemicals and electricity have been significantly reduced, reflecting both the elimination of all CFC solvent cleaning as well as the switch from a few large central cleaning stations to many small dedicated cleaning units.

III. DESCRIPTION OF PARTS CLEANED AT THE CHARLESTON PLANT

Most of the parts cleaned in the plant are for two assemblies: a fuel injector and an anti-lock brake system. Some parts are cleaned more than once during the assembly process, resulting in over 30 separate cleaning operations. The parts to be cleaned generally consist of mild steel, stainless steel, plastic, and rubber, and contamination to be removed typically incudes metal chips and fibres, grinding coolants, shop dirt, chemical residues, and fingerprints.

Cleaning operations at Bosch include both gross cleaning and precision cleaning. Gross cleaning is carried out on the open production floor, and precision cleaning is performed in the Class 10,000 clean room where final assembly takes place. Inadequate cleaning can compromise product performance and may result in failures. While the cleaning requirements are less than those of the semiconductor or disk drive industries, part cleanliness at Bosch means more than simple washing or scrubbing in soap and water. Particles larger than about 25 μm are of concern and are targets for removal by the cleaning process.

IV. PREVIOUS SOLVENT CLEANING TECHNOLOGY AT THE CHARLESTON PLANT

In 1988, all cleaning operations for manufacturing were performed using either CFC-113 or TCE. Typically these cleaning steps were carried out in large centrally located degreasers. Eight units used TCE and seven used CFC-113. These degreasers were off-the-shelf, commercially available units, and all included some form of solvent recovery. The units used combinations of spray and ultrasonic agitation in addition to vapour degreasing to dislodge the contaminants.

Both the TCE and the CFC-113 units served as general purpose cleaning stations for the various cleaning steps required in manufacturing. Parts passed through the cleaning station in their order of arrival, and the throughput time for baskets containing a total of 27 to 45 kg of parts was typically about 40 minutes. In this operating mode, solvent consumption in 1988 was 247,000 kg of CFC-113 and 60,000 kg of TCE.

V. OPTIONS FOR REPLACING CHLORINATED SOLVENTS

Options considered for replacing chlorinated solvents included "no-clean", other organic solvents, aqueous cleaning, and supercritical carbon dioxide. The most desirable option considered was the no-clean option. In evaluating no-clean manufacturing, the cleaning step was first examined to determine if cleaning was absolutely necessary. Sometimes the cleaning step can be eliminated with minor or no changes to the rest of the manufacturing process. Successful replacement of a chlorinated solvent with a no-clean process is a relatively rare event, but has large benefits in reduced costs and cycle time.

An example of this type of process change at Bosch was the replacement of solvent cleaning of a part between two machining steps. In the no-clean process, the oil-based lubricant is centrifuged off the parts, eliminating the wash and rinse cycles formerly used to clean the part. This eliminated a waste stream and, reduced the cycle time, chemical usage, and floor space required. The implementation of this no-clean technology was the result of an idea originated by shop floor manufacturing personnel.

For those operations for which no-clean technologies were not feasible, Bosch chose to bypass interim alternatives such as hydrochlorofluorocarbon (HCFC) solvents. It also was decided not to revert to the hydrocarbon cleaners used in earlier years. The Company's decision was to immediately address the long-term environmental issues associated with cleaning and to develop cleaning methods that would be as permanent as could be conceived under current knowledge and regulations.

The next option considered was aqueous cleaning. Aqueous cleaning with deionized water has proven very effective, especially when customized for a specific cleaning step on a specific part. The costs of deionized water cleaning become affordable when used in the limited quantities required by small, dedicated cleaning stations that incorporate reuse of the water before discharge. Bosch team members decided that parts cleaning could best be done with small custom cleaners dedicated to one or a few cleaning steps, which was a major change from the large central cleaners of 1988. This change eliminated any possibility of cross contamination, shortened cycle times, and allowed better matching of each cleaning process to the specific part and contaminants. The switch from large central cleaners to small custom units has improved part cleaning efficiency and reduced solvent losses. The introduction of single function washers for critical cleaning tasks was made easier by the fact that much of the existing cleaning equipment was 10 years old and in need of replacement. Particles larger than 500 μm were not being removed from parts in some of these units, and the Company felt that retrofitting or modifying the existing equipment would have been both expensive and short-sighted. Selecting new, customized equipment, however, required careful analysis of many cleaning steps.

The team reviewed other options for replacing chlorinated solvents, but did not select them for testing. Some, like supercritical carbon dioxide cleaning, were expensive and not production-ready. The primary reason for dismissing other options, however, was that aqueous replacement technology had more advantages and fewer potential drawbacks.

VI. CLEANING PROCESS SELECTION

Bosch uses two tests to evaluate the cleanliness of parts and the effectiveness of cleaning techniques. The first is a visual inspection. Parts are inspected for contaminants including fibres, dust, and machining debris. In a second test, lots are periodically audited by a five minute ultrasonic extraction of one basket of parts from the lot in petroleum distillate. The particles released during the extraction are collected on a filter with a 5 μm pore rating and weighed to assess cleanliness. Control charts plotting reject rates from both the visual inspection and the extraction test monitor the efficiency of the cleaning process.

Supporting tests may be carried out in a vendor's facility but vendor data have generally played a minor role in the replacement team's decisions. Time lapses between vendor cleaning and evaluation at Bosch hinder the use of this approach. New process evaluation at Bosch is typically performed on production equipment made available for tests during off-peak hours. Either an existing production unit is modified or adapted to a new process, or a prototype production unit is ordered from a vendor. Modifications and fine tuning are then carried out on the production scale units before the new process is incorporated into an ongoing production line.

VII. HARDWARE SELECTION

Solvent replacement selection at Bosch has always started with the selection of the cleaning process and associated hardware, such as ultrasonics, high-pressure spray, or turbo washing, rather than the selection of a cleaning solvent or fluid. The argument for this approach is that there are hundreds of chemicals to choose from but only a handful of cleaning processes.

To rapidly identify suitable aqueous cleaning hardware, Bosch first investigated off-the-shelf washing equipment. If off-the-shelf units proved ineffective or were not available, Bosch retrofitted existing equipment or engineered custom units of its own design. In one application, it converted a low-pressure spray washer to high pressure; in another, a high pressure unit was modified to use water instead of CFC-113. A turbo washer has also proven successful in aqueous cleaning of certain parts, but no single piece of hardware has been suitable for all cleaning applications.

Drying following wash and rinse was a sensitive issue for Bosch. Functional requirements typically require that all water be removed before the next operation. Removal of water by heating the parts often produced unacceptable spotting. Centrifuging at room temperature after aqueous cleaning has now become the drying technique adopted almost universally by Bosch. The centrifuges used provided the option of warm air circulation during the spinning, but this drying assistance has often not been necessary.

VIII. CHEMISTRY SELECTION

Compatibility of a chemistry with a part is determined by the Bosch chemical and metallurgical laboratories. These tests for chemical compatibility and absence of part degradation take 24 to 96 hours and are conducted before introducing any chemical into production. Safety considerations (flammability or toxicity) caused some solvents to be eliminated from consideration. The production floor itself then became the laboratory for final acceptance tests. Reasons for rejection included poor cleaning in production and objections from production personnel concerning solvent odour or part appearance after cleaning.

All but one replacement solution adopted to date has consisted of deionized water alone or deionized water with an alkaline cleaner. The specific additives and surfactants used in the cleaning steps were selected to be compatible with the part being cleaned, the soil being removed, and the cleaning equipment used. These decisions involved experimenting with various proprietary products to confirm rust protection and satisfactory soil removal. For example, oil-based lubricants are used for machining the parts. The parts are cleaned in aqueous systems with chemistries that allow the oil removed to separate from the water. Oil is then removed from the tanks in most operations by skimming or gravity separation in holding tanks, and is subsequently shipped off-site in sealed containers for disposal.

Parts cleaned by an aqueous replacement method typically had a different feel and appearance than those cleaned with a chlorinated solvent. They appeared dull and often had a different colour and some visible water spots. These obvious differences worried production personnel who were slow to accept the new cleaning process until they adjusted to the new acceptance tests and received assurances from the Quality Gauging Department that the new cleaning process was adequate. Only after a transition period, which varied from part to part and was as long as six months, did production personnel accept ownership of the new cleaning apparatus. Until this confidence was built, all breakdowns, equipment, and performance problems were immediately passed back to the replacement team. Once transfer of ownership was completed on one part, acceptance for other parts developed more easily and quickly.

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USE OF A LOW RESIDUE FLUX IN A MILITARY ELECTRONICS PROGRAM

I. SUMMARY

Rockwell Tactical Systems Division (TSD) and the U.S. Army Missile Command collaborated in a fifteen-month long evaluation of low-residue fluxes. The evaluation was specific to the options for the AGM-114 Hellfire Missile assembly line, and two of the new fluxes tested were eventually qualified for use. In July 1993, Hellfire became the first U.S. Army production program to implement low-residue flux technology. Today this technology is used in all of the assembly line's processes: wave soldering, lead tinning and hand soldering.

II. INTRODUCTION

In developing its ODS elimination program, Rockwell TSD first conducted an ODS usage survey. The survey revealed that its greatest use of ODSs involved rosin-based flux removal. 1,1,1-Trichloroethane was being used in batch degreasers, in-line solvent cleaners, and for manual brush cleaning, with consumption levels at 32,000 kg per year.

The objectives of the program were to:

- minimize the number of new chemicals brought into the division;
- keep capital expenditures for new equipment low;
- maintain weapon system performance and reliability; and
- minimize the impact of implementing a new cleaning technology on a production line that consistently produced defect-free circuit cards (CCAs).

Rockwell TSD produces several products for the Army and the Air Force, so in selecting a candidate production line for its first alternative technology trial, the company had many products to choose from. Since its highest volume product was the Hellfire Missile, this choice offered the most hardware for testing. Although all the Hellfire circuit cards are strictly through-hole (no surface-mount), some contain high density areas of moisture-sensitive circuitry. It was felt that Hellfire hardware would provide "worst-case" testing, and data collected during testing could be applicable to the other programs.

In formulating the ODS elimination program, a number of strategies were considered. The company first considered solvent-based technologies as a replacement for 1,1,1-trichloroethane. However, this proposition had several problems. For example, many alternate solvents:

- are hazardous to some degree;
- are expensive to produce;
- require special handling;
- require special storage conditions;
- require costly disposal techniques;
- are relatively new with little usage history;

- are undesirable for global warming, toxicity, or other reasons; or
- require expensive equipment for use.

Rather than focus on finding and testing solvent replacements for 1,1,1-trichloroethane, Rockwell decided that a preferable approach would be simply to eliminate use of rosin flux. Preliminary lab tests were performed with both no-clean (low-residue) and water soluble fluxes. Five non-rosin no-clean fluxes and six water-soluble organic acid fluxes were selected for the initial test. These preliminary tests evaluated:

- capability to solder plated-through-holes;
- effectiveness in tinning aged component leads;
- ionic cleanliness following a warm deionized water rinse; and
- solder mask effects.

The soldering performance for most of the flux samples was found to be adequate with two of the no-clean fluxes having outstanding results. While not expected to match the performance of the organic acid (water soluble) formulations, the no-clean fluxes surpassed the RMA-type flux used as a control. With this finding, Rockwell decided to only continue testing the top two no-clean fluxes, thereby avoiding the problems associated with removing organic acid residues caused by their corrosive characteristics.

One early finding was that the no-clean residues interfered slightly with the adhesion of some conformal coatings. This problem was resolved by washing the residues off with a saponified water cleaner prior to coating.

Based on this favourable preliminary data, a straw-man qualification plan was presented to the Army's Missile Command, Hellfire Project Office, and Product Assurance Directorate. The Army agreed to partner with Rockwell TSD and co-sponsor the qualification effort.

III. FLUX QUALIFICATION

A solder lab was established exclusively for the purpose of evaluating flux performance on coupons and circuit cards, providing the ability to conduct the study without exposing deliverable hardware to non-compliant chemicals. This lab was equipped with an Electrovert 400SV wave solder machine, a Branson precision batch cleaner, and a Zero Ion cleanliness tester. Manual soldering stations were set up to allow assemblers to try the new low residue cored-wire fluxes in simulated touch-up practices.

A test scenario was developed from available information. At the time of this evaluation design, no documentation existed with definitive DoD flux qualification requirements (although Bellcore had a TSY document that was available, and a draft of MIL-STD-2000B offered a test plan). Criteria was established and agreed upon by all Army and Rockwell team members. Following is a brief description of the tests that were performed in the qualification effort.

Surface Insulation Resistance (SIR) Testing. Pre-cleaned IPC B-24 Test Boards were prepared by fluxing and wave soldering with the comb patterns in the bottom-side and top-side configurations. Some test boards were cleaned using a saponified water wash; the rest were not cleaned. Hand soldering was also performed on test boards using the equivalent flux formulations in cored solder wire. RMA fluxed and soldered test boards were tested along with the new flux boards. Pre-cleaned non-soldered test boards were used as controls.

The test consisted of subjecting the boards to 85°C and 85% relative humidity conditions for 28 days with a 50-volt DC bias applied. A reverse bias of 100 volts was placed across the comb pattern and resistance measurements taken every 24 hours. All patterns were continuously monitored for any resistance breakdown caused by dendritic growth across conductor patterns. Boards successfully maintained SIR values well above the 1×10^8 ohm requirement.

Corrosion testing. This test was performed using the standard copper mirror method described in IPC-TM-650. Both fluxes were certified to be halide-free by their respective manufacturers.

Production hardware testing (CCA). Hellfire circuit cards with known sensitivities to moisture were assembled using the new fluxes. They were then subjected to the maximum expected system temperature (63°C) and 85% relative humidity for seven days, while under the 12 volt potential normally used in operation. No flux related anomalies were observed.

System Qualification Testing. As a final test for the Hellfire system, all CCAs were soldered with the new fluxes and assembled into the respective upper level modules using the no-clean wire solder. Modules were powered (18 VDC and 28 VDC) and subjected to 63°C and 85% relative humidity conditions for seven days. Following this treatment all modules were inspected and found to be functionally sound.

IV. FACTORY IMPLEMENTATION

On July 28, 1993, Rockwell converted the Hellfire production line to no-clean or low-residue flux. All rosin fluxes and rosin-cored solders were removed from the work stations. Several months prior to this activity, a task group from Operations had generated a comprehensive checklist of all items that would be affected by the flux change as part of an implementation plan. Rockwell addressed those processes affected by the flux and processes that relied on the use of 1,1,1-trichloroethane, which was to be eliminated after the new flux was introduced. The company's plan detailed each activity and listed its priority, the person(s) responsible for the activity, and a schedule for completing the activity.

Examples of items affected by the plan were:

- process sheets;
- training manuals;
- new chemical forecasts;
- waste disposal; and
- new process control procedures/equipment.

During the testing phase, it was determined that spraying was the optimum method to apply flux. Therefore, the receipt and installation of a spray fluxer was a major item on the list to be completed. Because low-residue flux is contained in a sealed reservoir, no significant evaporation occurs, reducing the need to monitor flux consistency. In addition, no flux need ever be discarded due to contamination or oxidation. Solder defects on the evaluation assemblies were very low (one to two defects per card), but higher than those with the RMA process (normally averaging 0.7 defects per card, or 99.9% defect free). Initially, the number of defects using the no-clean flux averaged around 6 per card. However, by fine-tuning the process over a four month period, defect levels were reduced to below the best results achieved with RMA-type fluxes.

The fumes from the new flux were found to be irritating to some employees. Fume extractors were installed on the soldering irons to rectify this problem. Many operators have found that in most cases, the new solder wire performed better than the RMA-cored wire, with the exception of tinning stranded wires. None of the low-residue fluxes have been found to adequately tin the inner strands and prevent "birdcaging."

V. OBSERVATIONS AFTER EIGHT MONTHS

The decision to use low-residue flux has proven to be the best option for Rockwell TSD. Defect levels have generally remained at or below those experienced with RMA fluxes. It is important to note the low-residue flux is less "forgiving" than rosin-cored flux. When parts were highly solderable, few problems with the low-residue flux were encountered; however, when parts were marginally solderable, low-residue flux performance was not so good. Problems with solderability typically have been traceable to isolated lots of boards or components.

As mentioned previously, solder-plated stranded wire is very difficult to tin with the new flux. The use of higher levels of flux solids and ultrasonic solder pots have failed to solve the problem. However, silver-plated stranded wires appear to tin very well.

Wave solder processes established for the rosin fluxes tend to evaporate the low-residue fluxes too quickly, resulting in a very dry board and poor through-hole wetting. In addition, the low-residue fluxes to increase the amount of solder dross generated. Dross reducers are being used to alleviate this problem. An inert atmosphere may also help, but has not yet been tested. The anticipated change in solder joint shape and brightness did not appear, so a recalibration of inspectors was not required. Finally, since the fumes were more irritating than those of the RMA-type flux, ventilation was increased, especially around the spray fluxer areas, and hand solder work stations.

In addition to being a technical success, this project has demonstrated the achievements possible by a cooperative effort between government agencies and industry.

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THE CLEANING CENTER SYSTEM OF SEIKO EPSON CORPORATION

I. SUMMARY

Almost all manufacturers share production responsibilities with suppliers. This allows them to "borrow" individuals with technical experience, maximizing the efficiency of their own human resources. Under this co-production arrangement, manufacturers can make high-quality products faster and at lower cost than otherwise possible. This arrangement also lends itself to solving shared problems, including environmental problems such as ozone depletion.

Without such cooperation, small- and medium-sized companies may have difficulty in finding ways to establish alternative technologies and introduce new equipment without interfering with production. In addition, they may be hampered by:

- poor investment payback;
- limited floor space;
- lack of technical expertise regarding cleaning machinery and solvents, making them overly reliant on equipment/solvent manufacturers for technical assistance; and
- a small labour pool with few engineers.

Given these limitations, small- and medium-sized companies may not be able to eliminate use of ODS on their own. Moving to alternative cleaning processes is not simply a matter of transferring technology from larger companies. The Cleaning Center System of Seiko Epson is designed to address these problems.

II. INTRODUCTION

Like many other small- to medium-sized companies, Seiko Epson has opened a cleaning center equipped with non-ODS cleaning equipment. Seiko Epson has invited many of its parts suppliers to share the use and expenses of this cleaning center. The center is designed to eliminate ozone-depleting substances from production processes.

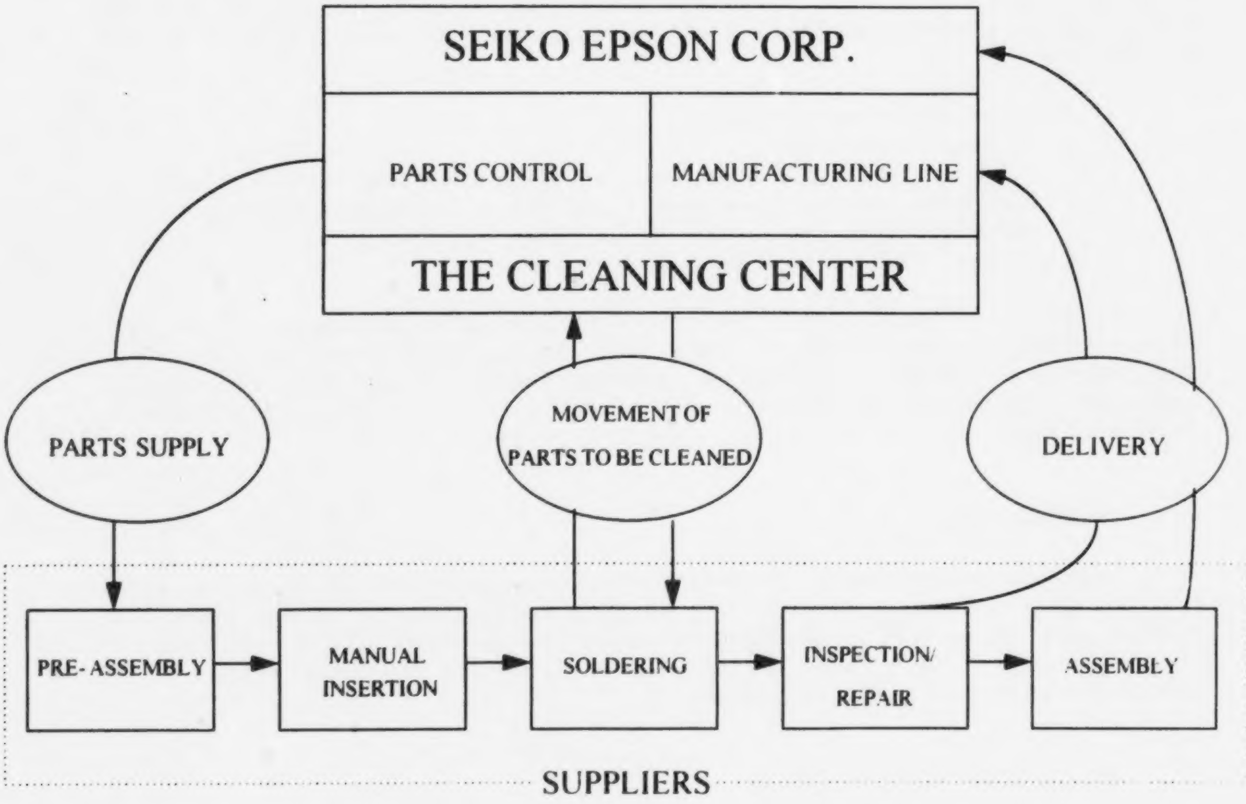
III. THE CLEANING CENTER SYSTEM

The Cleaning Center is a way to share ODS-free cleaning equipment with suppliers of Seiko Epson. The primary benefit of a common cleaning center is an opportunity to share costs while preventing pollution. The system is described in Figure XI-5 using the printed circuit board manufacturing process as an example.

First, Seiko Epson supplies the subcontractor (supplier) with printed circuit board (PCB) parts. The subcontractor then mounts these parts on PCBs. Next, the mounted PCBs are transported to Seiko Epson to be cleaned by Seiko Epson's ODS-free cleaning process. After the boards have been cleaned, the subcontractor transports them back to its own plant, inspects them and makes

Figure XI-5

SEIKO EPSON CLEANING CENTER SYSTEM


SEIKO EPSON CORP.
PARTS CONTROL
MANUFACTURING LINE
THE CLEANING CENTER
PARTS SUPPLY
MOVEMENT OF PARTS TO BE CLEANED
DELIVERY
PRE-ASSEMBLY
MANUAL INSERTION
SOLDERING
INSPECTION/ REPAIR
ASSEMBLY
SUPPLIERS

any necessary repairs. Finally, the finished products are delivered to Seiko Epson.

In the present arrangement, the ODS-free cleaning equipment is used 24 hours a day. From 8:30 AM to 5:00 PM, products entirely manufactured by Seiko Epson are cleaned. The remainder of the day is scheduled for supplier use, with employees of Seiko Epson running the cleaning operation. Suppliers can deliver dirty parts and pick up clean parts 24 hours a day.

The layout of the cleaning operation is shown in Figure XI-6. Some general technical information about the cleaning equipment is given below:

- System size: 1.6 m X 5.86 m.
- Conveyor speed: 0.8 m/min.
- Cleaning capacity: 1.6 to 1.7 million parts/month.
- Use restricted to glass epoxy circuit boards with maximum width of 400 mm constructed using lead wires or SMT.
- Parts can extend up to 80 mm from the surface of the conveyor belt.
- Pure water feeding device: 30 litre ion replacement tower.
- Pure water control ration resistance value: 1 us/cm.
- Two-tiered float switch used to monitor water levels in each bath.

The bath configuration is in-line and uses a conveyor belt. It has showers that simultaneously clean the top and bottom surface of printed circuit boards. The system has three zones - saponification, rinsing, and drying. It uses a closed system so wastewater treatment is not required, and the cleaning machine works for more than one specification of circuit board. The speed of the cleaning machine can be adjusted such that only one person is required for normal operation of the system.

IV. ISSUES

Each supplier is responsible for controlling its products. A cleaning order is attached to each lot of products and all work is carried out on the basis of the order.

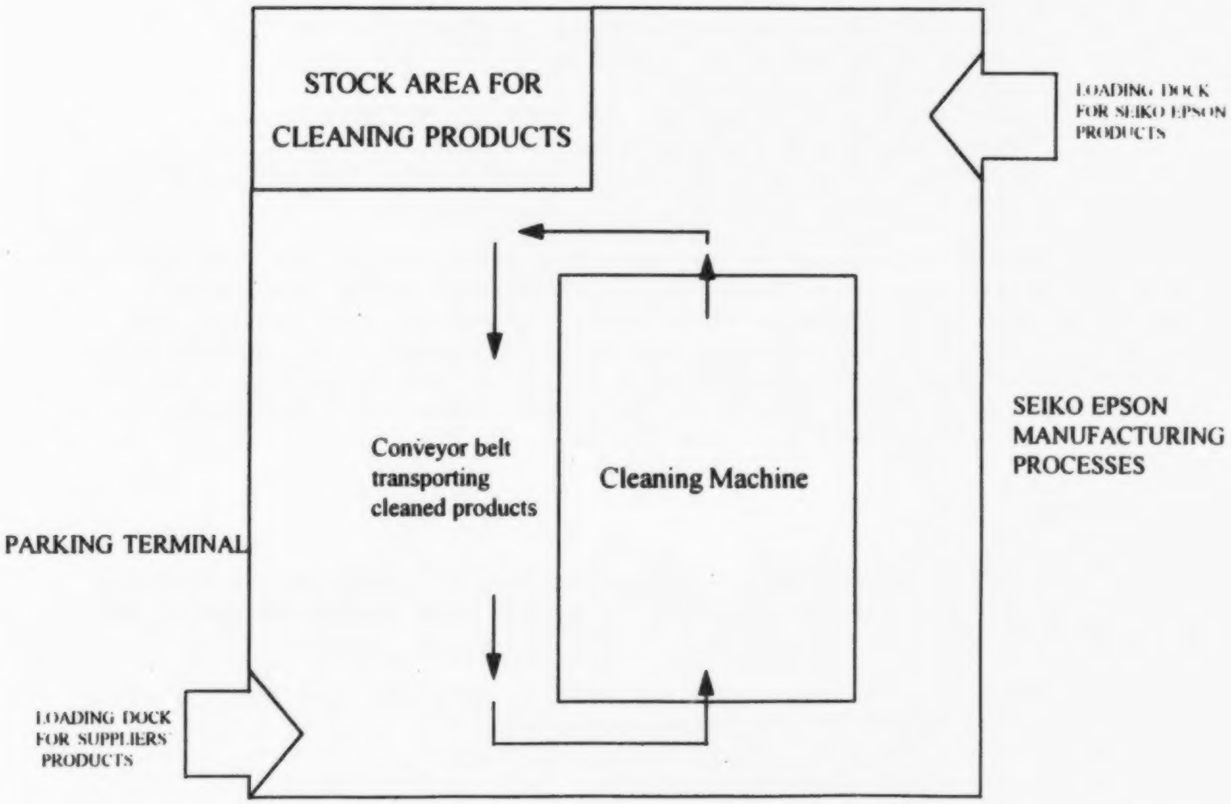
Some advantages of the system and equipment-sharing arrangement include:

- high equipment investment efficiency;
- better cleaning results than old system;
- consistent cleaning quality;
- lower cleaning costs; and
- lower expenditures for energy and solvents.

Disadvantages include longer lead times and higher transportation costs since suppliers are required to transport their products to the cleaning center. Prior to their use of the Seiko Epson Cleaning Center System, the cleaning process was integrated into their own manufacturing system. The Cleaning Center was designed for 24-hour-a-day operation to help alleviate these higher costs.

Figure XI-6

CLEANING CENTER LAYOUT


STOCK AREA FOR
CLEANING PRODUCTS
LOADING DOCK
FOR SEIKO EPSON
PRODUCTS
SEIKO EPSON
MANUFACTURING
PROCESSES
Conveyor belt
transporting
cleaned products
Cleaning Machine
PARKING TERMINAL
LOADING DOCK
FOR SUPPLIERS
PRODUCTS

Prior to the Cleaning Center opening, suppliers picked up Epson-supplied parts and delivered finished products. Under the common cleaning center arrangement, however, they were initially required to make an extra trip in the middle of the production process to have their products cleaned. This factor increased their transportation costs. To maintain transportation costs at the previous level, Seiko Epson adjusted its delivery schedules so that a truck runs a regular route that covers all suppliers twice a day. In the first round, Seiko Epson delivers cleaned parts to the suppliers and picks up finished products. In the second round, Seiko Epson delivers parts to be packaged and picks up boards to be cleaned.

V. CONCLUSION

Smaller enterprises may sometimes need the cooperation of larger companies if they are to achieve a total phaseout of ODS before the January 1, 1996 deadline. Seiko Epson believes the common cleaning center arrangement is an effective way to help small- and medium-size companies eliminate ODS.

Seiko Epson also believes that the Cleaning Center System can be easily applied to many industries in many countries. The company recommends retaining technical experts in the various relevant fields during the transition period to efficiently manage any problems that may arise.

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THE ODS-FREE VERIFICATION SCHEME FOR SINGAPORE INDUSTRY

I. INTRODUCTION

The project to develop an ODS-Free Verification Scheme was begun in June 1993 by the Singapore Institute of Standards and Industrial Research (SISIR) as a means for companies to demonstrate (via third-party proof) that they are not using ozone-depleting substances in their manufacturing processes. The Scheme is open to local manufacturers in Singapore and has the support of the Singapore Economic Development Board (EDB) and multinational companies (MNC) through the Local Industry Upgrading Program (LIUP). MNCs and large local companies contribute program managers to LIUP in the planning and implementation of programs for upgrading the technology and business of local vendors.

The SISIR Scheme provides several services to companies.

- It provides public recognition for companies who have phased out ODS in their manufacturing processes.
- It provides MNCs and international purchasing offices (IPO) in Singapore with a source of independent verification and eliminates the potential for multiple audits.
- It makes it easier for participating companies to export products to countries such as the U.S., since the U.S. Clean Air Act requires the labelling of imports that are manufactured using substances which are harmful to the ozone layer.
- It provides technical assistance from SISIR to companies who are switching to ODS-free alternatives as well as consultation on the means to obtain verification.

SISIR's Chief Executive, Mr. Khoo Lee Meng, believes that no other signatory to the Montreal Protocol has a national verification scheme similar to that established in Singapore.

II. REASONS FOR THE ODS-FREE VERIFICATION SCHEME

The industry's need for an independent, third-party verification scheme was identified through the LIUP's network of MNC-partners. The necessity for this type of verification scheme arose as a result of the following issues:

- The current worldwide 'green' movement.
- The imposition of the ODS phaseout schedule under the Montreal Protocol.
- Many of Singapore's trading partners require imports to be ODS-free.

III. VERIFICATION PROCEDURE

Companies participating in the verification scheme follow an established procedure:

- The applicant company submits flow charts, discloses the chemicals used in the manufacturing process and indicates if the company has obtained or is seeking ISO 9000 certification.
- SISIR conducts audits of the company. SISIR examines supporting documents and documentation procedures, and tests samples of chemicals employed in manufacturing to verify that no ODSs are being used.
- Following initial certification, the company is periodically surveyed to ensure compliance with the terms and conditions of the Verification Scheme.

The verification procedure costs local companies between U.S.$4,000 and U.S.$8,000. To help local companies defray the cost of verification, the EDB offers financial assistance under the Local Enterprise Technical Assistance Scheme (LETAS). Grants of up to 70% of the cost are awarded to companies who seek verification before December 1994. After December 1994, grants of up to 50% of the cost will be available to companies.

IV. SUCCESS OF THE VERIFICATION PROGRAM

Companies cited a variety of reasons why they participated in the verification program. For example, New Electronic Technology joined the Scheme because several of its customers ship their products to the United States and these products need to be labelled. Micro-Team Industries, which used solvents to chemically coat electronic parts and other objects with metal, stopped using these solvents in order to protect the health of their workers. SEA Trading Co. said they participated to demonstrate to the public their belief that environmental protection is important.

Since the verification program began, more than 40 companies have expressed interest in seeking verification. As of March 1994, eight companies had received verification. As of August 1994, Leica Instruments, a multinational company which produces precision optical components, had been successfully audited. Another multinational company, SONY Display Device, which produces colour television tubes, is ready for the pre-award audit. In addition, thirty companies are currently in various stages of application for verification.

The eight companies which have received certification for having stopped using ODS in their manufacturing processes are primarily plastics moulding and electronics components manufacturers. Six of these eight companies are in the EDB's LIUP:

- Hi-P Tool & Die
- Next Electronic Technology
- Mould Technic
- Micro-Team Industries
- Joetsu Engineering Plastic
- Chartered Electronics Co.

The remaining two companies which received certification are:

- Singapore Asahi Chemical & Solder Industries
- SEA Trading Co.

Table XI-1 presents more detailed information on each of these eight businesses.

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Table XI-1

SUCCESSFUL ODS ELIMINATION IN SINGAPORE

Name of Company	No. of Employees	Type of Business
HI-P Tool & Die Ltd.	75	Mould design & fabrication for injection moulded plastic parts for electrical industries.
Next Electronic Technology Pte Ltd.	303	Contract manufacturing of PCBs, flexible circuits, & ceramic hybrid modules.
Mould Technic Pte Ltd.	56	Design & fabrication of precision moulds and plastic injection moulded parts primarily for medical industry.
Micro-Team Industries Pte Ltd.	33	Electrolysis nickel plating of metals and plastics, chemical conversion of metals, & passivation of steels.
Joetsu Engineering Plastic Pte Ltd.	15	Mould design and fabrication, precision engineering plastic, injection moulded parts for audio, computer, electrical, & electronic component manufacturers.
Chartered Electronics Co. Pte Ltd.	110	Wire harnessing and electronic parts assembly.
Singapore Asahi Chemical & Solder Industries Pte Ltd.	40	Manufacturing solder paste, bars, wires, anodes, soldering fluxes, and chemicals for electronics industry.
SEA Trading Company Pte Ltd.	38	Manufacturing polystyrene disposable products.

ELIMINATING THE USE OF ODSs IN SWEDEN

I. INTRODUCTION

In 1988 the Swedish Government, after consultation with industry, industrial and trade associations, and concerned agencies, passed a law mandating a complete phaseout of ozone-depleting solvents (ODS) in all end-uses by the end of 1995. This was the first complete phaseout schedule proposed worldwide.

The task of implementing the overall phaseout of ODSs in Sweden was delegated to the Government to the Swedish EPA (SNV). In light of the global nature of the hazardous impact of ODSs, a vital component of the Swedish strategy was to transfer experiences from the Swedish phaseout to other countries and thus strive for an early global phase out of ODS substances.

II. EVALUATING ODS USE

It was believed that although the amount of ODS used and emitted in Sweden was small, and the direct impact on improvement of the ozone layer would also be small, the diversity of the Swedish industrial structure and application areas for the CFCs was as complex as any of the larger users of ODS. Consequently the experience gained by Sweden from the phaseout would be valuable to other major users.

Of the various ODS-use areas, the solvents sector is generally considered to be among the most sophisticated and complex. The major users of ODS-solvents are the electronics, telecommunications, aerospace, defense and general engineering sub-sectors. Consequently, ODS solvents were believed to be difficult to replace. The Swedish Legislation called for the solvent sector to be addressed first and mandated a 100 percent phaseout by January 1, 1991 -- four years ahead of the national phaseout.

III. PHASEOUT PROGRAMMES

The SNV developed the solvent phaseout implementation programme by cooperating with the concerned Nordic industries in a number of R&D programmes. These programmes called for the assessment of alternatives and investments in some new technologies. Two major programmes were the TRE (Teknik fös Ren Elektronik) and AMY (Avfetlning av Metallytor) projects. These projects addressed alternatives and reliability issues. The US$3.5 million programmes were co-financed by industry (e.g., electronics, telecommunications, aerospace companies -- Ericsson, ABB, FFV, SAAB, Electrolux, NFT, Norsk Hydro); governmental authorities (e.g., SNV (Sweden), The Norwegian State Pollution Control Agency, The Danish Ministry of Environment, The Swedish Defence Procurement Authority); research and development institutes (IVF (Sweden), YKI (Sweden), MRI (Sweden), EC (Denmark), VTT (Finland); industry associations (MF (Sweden); and a financial institution (The Nordic Investment Fund).

The programmes were carried out with active participation of all involved parties and began with a number of awareness workshops and conferences. A hallmark of the programmes was to exclude chemical and equipment supplier financing and rely only on industrial user and agency financing. It was the opinion of industry that this approach would maintain the integrity of the programme and its undertaking.

The programme was initiated in 1988 and terminated in 1993. The activity helped contribute in a significant manner to the Swedish industry's virtual 100 percent phaseout of CFC and 1,1,1-trichloroethane use as solvent as mandated by 1991 and 1995, respectively. In the case of Sweden, only SNV has had the authority to issue exemptions for the use of CFC as a solvent after the phaseout date. As of January 1, 1991, exemptions had been granted for only a few hundred kilogrammes of CFC usage. These exemptions have not required renewal. In the case of 1,1,1-trichloroethane, exemptions for a few hundred kilogrammes have been submitted to date and are under review. These exemptions, if granted are expected to be valid only for 1995.

IV. INFORMATION DISSEMINATION

A vital component of the phaseout strategy was to disseminate the results of the Swedish phaseout experience to outside parties and to work for a more rapid global phaseout than that agreed upon by the initial Montreal Protocol. This effort was executed by participation in the UNEP technical assessment committees, e.g., the Solvents, Coatings, and Adhesives Committee. The 1989 committee included industry and government participants from the Canada, Japan, Sweden, Switzerland, U.K., and U.S. The approach adopted for the assessment was to assess all alternatives and, on site, examine the alternatives in operations to assess the feasibility of a complete phaseout worldwide by the year 2000 in the solvent sector.

The second committee was convened in 1991 and included representatives from major chemical companies. The mandate for the second committee called for a close examination of the possibility of a more rapid phaseout despite the inclusion of 1,1,1-trichloroethane which at one stage was considered as an alternative to the use of CFC as a solvent. The replacement of 1,1,1-trichloroethane was considered especially difficult due to its large and diverse use. The committee examined alternative operations on site for a variety of applications and the conclusion drawn by the committee was that, provided sufficient funds and resources were available, a complete phaseout was possible by the year 1996 with a ten-year grace period for the developing countries.

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NON-ODS SUBSTITUTES FOR WAX ELIMINATION AT TOSHIBA CORPORATION

I. SUMMARY

Manufacturers have developed vinyl-copolymer type masking materials that can be removed by hand-wiping with dry rags or rags dipped in organic solvents such as methyl ethyl ketone (MEK). The use of these materials can be a practical and easily-implemented alternative to the use of wax masking materials and ozone-depleting solvents (ODSs) at aircraft maintenance facilities.

II. INTRODUCTION

Aircraft parts and electric equipment parts are typically covered with a protective mask prior to chrome plating to restrict electroplating to the unmasked locations on the parts. At Warner Robins Air Logistic Center's Plating Shop, microcrystalline beeswax was used in combination with electroplating tape to mask parts prior to chrome plating. Before converting to non-ODS technology, Warner Robins removed this wax by placing the parts in a vapour degreaser after plating. After several hours, the heated 1,1,1-trichloroethane vapour dissolved the wax. The facility's two vapour degreasers were able to dewax approximately 500 chrome-plated parts per month. During the process, wax would accumulate on the bottom of the degreasers and form a thick sludge. The degreasers required weekly cleaning to maintain their efficiency and to prevent accumulation of the wax sludge. This cleaning used approximately 1,514 litres of 1,1,1-trichloroethane per week to remove approximately 1,136 litres of sludge that was recycled at another location on-site. The use of 1,1,1-trichloroethane has been discontinued in this application and wax is now removed from aircraft parts using steam cabinets equipped with numerous high pressure nozzles.

III. THE ALTERNATIVE SELECTION PROCESS

Electric companies have been using vinyl-copolymer type masking materials for years in the same application as Warner Robins. This type of material can be removed by hand easily without the use of solvents. Some aircraft maintenance engineers previously considered vinyl-copolymer type materials to be less effective than wax in terms of productivity and reliability, especially on narrow areas or complicated surfaces. However, vinyl-copolymer type masking agents have been developed recently that alleviate these concerns.

Table XI-2 shows an example of the composition of vinyl-copolymer type masking agents. Many electrical engineers consider vinyl-copolymer type materials to be better than wax in operating characteristics, since vinyl-copolymer type materials can be applied with a brush or a spray and dried at room temperature. Narrow areas can be coated carefully and with precision, whereas parts must be dipped when using wax as a masking agent. One problem involved in using vinyl-copolymer type materials, however, is its lower adhesive strength.

Table XI-2

COMPOSITIONS OF VINYL-COPOLYMER-TYPE MASKING AGENTS

Compounds	Red (Precoat:Sticky)	Green (Maincoat:Normal)
Resin	Vinyl chloride/ Vinyl Acetate Copolymer	
Softener	DOA (Dioctyl Adipate)	
Plasticizer	Epoxytriglycerol	
Stabilizer	Dibutylbis (Lauroyloxy) stannate	
Colouring Dye	Oil Red	Phtalocyanine Green
Surface Lubricant	Silicone	
Antifoaming Agent	Silicone Type	
Solvents	Acetone 14-15%	
	MEK (Methyl Ethyl Ketone) 30%	
	Methyl Isobutyl Ketone 17%	
	Toluene 5%	

Occasionally, vinyl-copolymer type films peel off because of bubbles generated by electrolysis, indicating that it may be necessary to reinforce some areas with electroplating tape. Another method to prevent peeling is by double-coating the part. In this process, a sticky precoat containing toluene as a solvent is applied first, and then the main coat is applied.

IV. CONCLUSION

Vinyl-copolymer type materials should be a convenient material to use in masking parts prior to chrome plating activities. The use of these materials is expected to increase as more aircraft maintenance facilities are convinced that vinyl-copolymer type materials will perform as well as wax in terms of workpiece productivity and masking reliability. It is important to establish evaluation methods and also conduct additional field testing of these masking agents to determine their effectiveness.

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USING NEW TECHNOLOGIES TO SOLVE UNIQUE PRECISION CLEANING OPERATIONS: THE ELIMINATION OF OZONE-DEPLETING SOLVENTS FROM THE AEROSPACE GUIDANCE AND METROLOGY CENTER NEWARK AIR FORCE BASE, OHIO

I. INTRODUCTION

The Aerospace Guidance and Metrology Center (the Center) operates a major repair facility at Ohio's Newark Air Force Base. The Center's primary purpose is to repair inertial guidance and navigation systems used by U.S. Air Force aircraft and missiles. These sophisticated systems contain complex electromechanical components that are extremely susceptible to contamination. As a result, the Center operates a variety of general and precision cleaning systems, all of which are located in strictly controlled environments.

Prior to 1988, the Center consumed approximately 1,250 metric tons (MT) of CFC-113 and smaller quantities of 1,1,1-trichloroethane (TCA) annually during the precision cleaning of various electromechanical components. Both ozone-depleting solvents were used to remove oil, dirt, fingerprints, and other contaminants deposited on electromechanical components during their operation and repair.

II. AQUEOUS ALTERNATIVES

Following the signing of the Montreal Protocol in 1987, the Center began its search for CFC-113 and TCA alternatives. In order to avoid possible future regulatory constraints, the Center sought the most environmentally benign solution to its cleaning problem. The Center, which had access to an inexpensive water supply and a local municipal wastewater treatment plant, began to investigate aqueous cleaning technologies. Aqueous detergents were known to be environmentally friendly and are usually nontoxic or low in toxicity. An independent consultant hired by the Center to conduct a study of the impacts of aqueous cleaning concluded that there would be no need for wastewater pretreatment if the Center converted to aqueous cleaning processes. In addition, aqueous products do not contribute to ozone-depletion or global warming, and are not classified as volatile organic compounds (VOCs).

Since process development began in 1987, the Center has replaced 43 percent of its ODS-based cleaning with aqueous cleaning technologies, and has installed 17 aqueous cleaning stations, most of which include a variety of aqueous cleaning devices. Many of the cleaning stations contain ultrasonic equipment, and each has access to a heated water supply and compressed-air drying system. To ensure consistent precision cleaning and spot-free drying, the Center uses only high quality deionized water that is filtered and recirculated through the deionizing system to prevent the build up of particulate and biological film. The water supply can be heated and delivered to the appropriate cleaning station at temperatures ranging from 16°C to 68°C. The compressed air is filtered and delivered through a hand-held blowing device at a gage pressure of 414 kPa and a flow rate of 0.0084 m^3/sec. This method of drying parts removes moisture in a consistent and spot-free manner at least as rapidly as CFC-113 evaporates from the same parts when dried in still air. Using this system, the Center is confident that at least 95 percent of its ODS-based cleaning methods will be replaced by aqueous technologies by 1995.

The Center scrutinizes every aspect of its existing cleaning methods to ensure that aqueous alternatives are tailored perfectly to the application. Because components repaired and cleaned by the Center are constructed from a variety of different materials including jewels, adhesives, plastic, copper, iron, beryllium, and aluminum, personnel must adjust the parameters of each alternative cleaning process so that the process satisfactorily cleans the specific part without damage. Consequently, the aqueous detergent, the length of the drying and rinsing cycles, the temperature of the water, and the design of the cleaning machine are all subject to change from one process to the next. For this reason, the Center develops each new cleaning process individually. Developing an aqueous method of cleaning gyroscope components, for example, required testing various water temperatures to ensure that the epoxy used to bind the gyroscope components was not damaged during the cleaning process.

The Center will not convert to aqueous alternatives unless it is convinced that the new process will provide a final product at least of a quality equal to that of the ODS-based process it replaces. Remarkably, the Center has found that product quality usually increases after converting to aqueous cleaning. Aqueous methods of cleaning precision bearings, for example, increased their acceptable product yield by 25 to 65 percent compared to bearings cleaned with CFC-113. Another remarkable trend that has occurred at the Center following conversion to aqueous cleaning methods is an overall decrease in product processing times. For example, the total processing time required to clean one of the gyroscopes repaired at the Center was reduced by 7.1 percent after switching from CFC-113 to aqueous cleaning, a reduction equivalent to 16 hours of labour. The Center also found that aqueous cleaning processes are much less expensive than equivalent ODS cleaning processes. The reduction in CFC-113 use that has occurred at the Center as a result of its current 43 percent conversion to aqueous cleaning is equivalent to an annual reduction of $1.8 million in operating costs. The investment cost for a 100 percent conversion to aqueous cleaning is not expected to exceed $1.5 million. Complete conversion to aqueous cleaning will also reduce energy consumption and hazardous waste disposal at the Center.

III. NONAQUEOUS ALTERNATIVES

Converting ODS-based cleaning processes to aqueous-based cleaning processes has numerous advantages. Unfortunately, it is not possible to use aqueous processes for certain cleaning applications. For these processes, the Center evaluated and selected nonaqueous alternatives on the basis of cleaning performance, environmental impact, cost effectiveness, and employee health and safety. Using these criteria, the Center identified alcohol, volatile methyl siloxanes, perfluorocarbons, and supercritical fluids as potential nonaqueous technologies that can be used to replace ODS-based cleaning processes. These four technologies have no ozone-depleting potential (ODP) and are either nontoxic or have very low toxicity. Each nonaqueous technology, however, has one or more major drawbacks.

Alcohol technologies can be used by the Center to remove mildly activated rosin flux residues (a by-product of soldering) deposited on fragile gyroscope wires. Aqueous cleaning is not possible because the wires are so fragile that the surface tension of water will deform them. The primary concern with using isopropyl alcohol (IPA) is its flammability. For this reason, the Center has selected a cleaning system designed with safety features that allow its use with pure IPA in normal production areas without special precautions. IPA, however, is a VOC whose emissions are subject to control in many localities.

The Center is investigating the use of volatile methyl siloxanes for removing a variety of contaminants, including difficult-to-remove phenylmethyl silicone which is used as a damping fluid in some gyroscopes. Like IPA, methyl siloxanes are flammable materials that require special handling and disposal. Unlike IPA, however, methyl siloxanes are quite expensive.

Repairing inertial navigation systems requires extremely critical precision cleaning, and the Center obtained assistance from the Small Business Innovative Research Program (SBIRP) to develop solutions to this problem. SBIRP funding is available to the Department of Defense (DoD) as a means of encouraging small U.S. businesses to apply their innovative concepts to solve DoD problems. The Phasex Corporation was selected to assist in a project which involved the removal of a heavy phenylmethyl silicone oil from a complex accelerometer assembly. The assembly must be cleaned in one piece, which is difficult to achieve with CFC-113 and impossible to achieve with an aqueous process. Phasex considered both carbon dioxide and ethane as part of a supercritical fluid (SCF) cleaning process to remove silicone oil from the assembly. After thorough research and testing, ethane was found to be superior to carbon dioxide as a supercritical solvent for removing the oil. Although ethane is flammable, it, unlike carbon dioxide, has no global warming potential. In general, SCF technology is effective at removing oil and grease from components or assemblies whose parts are not harmed by temperature and pressure applied during the process. Phasex, working with process experts at the Center, designed and constructed a SCF cleaning station which can operate with either carbon dioxide or ethane. The cleaning delivers a superb product, but will not be used for applications which can be performed with cheaper or more environmentally benign technologies.

A second SBIRP project was aimed at developing a perfluorocarbon technology for the removal of fluorinated oil and particulate from inertial components. Entropic Systems was selected to lead the project, and developed an ultrasonic process that uses a perfluorocarbon with a fluorinated surfactant for cleaning. The process removes particulates better than CFC-113, and has been incorporated into a low-emission cleaning station that began operation in 1994. Because of the high cost and high global warming potential of perfluorocarbons, the Center plans to use the new technology only when other alternatives are not capable of achieving the desired level of cleanliness.

IV. CONCLUSION

Through the extensive research, development, and implementation of alternative manufacturing and cleaning methods, the Aerospace Guidance and Metrology Center has dramatically reduced its use of CFC-113 and TCA in the last five years. The Center plans to continue reducing its use of ozone-depleting solvents to achieve a complete phaseout in early 1995.

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Case Study: Vibro-Meter SA, Villars-sur-Glâne, Switzerland

I. INTRODUCTION

Vibro-Meter SA is a manufacturer of vibration detectors for gas turbines and similar applications, as well as sensors for pressure, flow etc. They also design and manufacture the associated electronics for these sensors. Because its products are used extensively in the aerospace industry, high-reliability is a requirement for all finished products.

The electronics assemblies use conventional, surface-mount, and mixed technologies with small physical dimensions and high component densities on multi-layer boards. Prior to 1992, wave-soldering was performed exclusively with a medium-solids RA flux and reflow soldering used an RMA solder-paste. The cleaning process used a CFC-113/alcohol azeotrope in an open-top manual vapour phase degreaser with water-cooling and two solvent tanks. Initially, no specific precautions were taken to minimise solvent vapour emissions. Therefore, the solvent consumption per unit area of cleaned boards was relatively high, especially considering that the production rate was moderate and inconsistent.

In early 1992, it was realised that the Swiss Federal Ordinance on Substances Dangerous to the Environment was legislating a phase out of the use of CFC-113 and 1,1,1-trichloroethane for industrial purposes by December 31, 1992.

II. THE SEARCH FOR A SUBSTITUTE

A study of substitute processes (materials and equipment) was undertaken and it became apparent that all the technically and economically viable cleaning methods used water, at least in the final phase of cleaning. Given the stringent regulations on heavy metals, (0.1 mg/l for lead, 1 mg/l for copper, and 2 mg/l for tin) in water quality in the Swiss Federal Ordinance on the Discharge of Waste Waters, the prospect of using water in the cleaning process was not initially attractive. In addition, the Cantonal (State) authorities wished to apply Federal recommendations for pH and BOD_5 to the wastewater. As the production level at the Vibro-Meter facility was fairly small, a capital-intensive or consumable-intensive wastewater treatment plant could not be justified.

After a quick examination of the possible alternatives, the list was narrowed to the following:

- "No-clean" soldering
- Water-soluble flux with aqueous-cleaning
- Saponification-removal of rosin fluxes, plus aqueous cleaning
- Hydrocarbon/surfactant removal of rosin fluxes, plus aqueous cleaning

"No-clean" techniques were rejected because of worries about consistency in process control and materials. An examination of available machinery for aqueous cleaning revealed that there were three types readily available: a modified 'dishwasher' type which could have limited throughput and relatively high water and energy consumption; a 'high-throughput' batch machine; and a number of conveyorised "in-line" machines.

III. AQUEOUS CLEANING OF PRINTED CIRCUIT BOARDS

One 'high-throughput' batch machine vendor offered a solution which satisfied all of the company's requirements in terms of capacity, technical feasibility, and water and energy consumption. With the assistance of information from the vendor, this system was accepted by the authorities on condition that analyses taken at the outfall showed acceptable pollutant levels according to Federal and Cantonal regulations. The only exception allowed by the authorities was for the stainless steel machine to be cleaned periodically with a short-chain linear carboxylic acid product whose working solution could have a pH lower than the permitted limit of 6. This cleaning process involved a maximum of 50 litres of solution once per month.

The system has a "hold tank" after soldering with a water-soluble flux or paste. All the assemblies coming out of the wave-soldering machine or the reflow oven were immediately placed in a polyethylene tank containing a weak aqueous chelating solution. This room-temperature solution removed most of the residues from the warm assembly while they were still liquid and took them into solution. The slight alkalinity of the solution (pH about 9) also prevented the highly acidic flux residues from attacking the solder surface, ensuring an easily inspectable solder joint. In addition, the chelating action solubilised the heavy metal salts resulting from the reaction between the flux and the metal oxides on the solder surface or the component leads. Foam reduction was yet another advantage of the process. The result of the "hold tank" was that less than 5-10% of the normal amount of contaminants were present after the solution left the tank. The water in the "hold tank" is tested by a dye which changes colour if the pH drops excessively and by a visible precipitation if the heavy metal content exceeds the chelating power of the solution.

The cleaning machine has a 50 litre tank which is initially filled with tap or deionised water. A high-power pump sprays the water onto the assemblies, which are held near-vertically in baskets, via jets from linearly oscillating spray bars held above and below the parts. After the wash cycle, the boards are sprayed in open circuit with deionised water. This water may have 3-5% isopropanol added. The rinse spray bars are separate from the wash spray bars. The oscillation of the spray bars ensures approximately eight to ten separate spray rinses at any given point on an assembly during the 30-45 second rinse period. The rinse water is uncontaminated when it initially reaches the assemblies. After the rinse cycle, the lightly contaminated rinse water falls into the wash-water tank and dilutes the contents. Wash water is normally only drained at the end of each week.

Once rinsed, the baskets are transferred into an separate drying machine. The drying machine utilizes very-high-speed rotary air knives which mechanically blow off the excess water and contaminants (approximately 90-95% of the quantity at the cleaning machine exit) within a few seconds. The residual moisture is then evaporated, requiring comparatively little energy. It is possible to clean and dry a basket with 1-2 m^2 of assemblies every 6-8 minutes.

The residues from the new cleaning system have been shown by Contaminometer tests to be better than $^1/_5$-$^1/_{10}$ of the residue levels from the previously used CFC-113 cleaning system, and well under the limits specified by military standards. The only negative aspect that has arisen is the need to be more careful about selecting components with the cleaning process in mind. Although an adaptation period was needed to achieve optimum performance, the use of water-soluble chemicals has made the soldering process marginally better, resulting in a small reduction in the amount of rework required.

No significant problems have arisen as a result of wastewater generation. The contents of the hold-tank are drummed disposed of as a special hazardous waste after the tank is emptied periodically. The costs of treating a lightly basic aqueous solution with heavy metals are relatively small.

The company has found that the equipment selected is particularly economical in terms of both deionised water and energy use with no overall cost increase compared to CFC-113. Typical consumption is 5 litres and 700 kWh per square metre of assemblies, respectively.

IV. CONCLUSIONS

This case study provides an example of the defluxing of high-reliability assemblies in a small-to-medium sized enterprise, respecting all the environmental criteria in a country noted for severe restrictions. The same techniques may be applied in both developing and developed nations. The capital cost required for the conversion is approximately US$40,000.

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APPENDIX C[1]

RECOMMENDED GUIDELINES AND CONTROL ACHIEVABLE WITH BEST AVAILABLE TECHNOLOGY (BAT) FOR VOLATILE ORGANIC COMPOUND (VOC) SOLVENT-BASED CLEANING

I. GENERAL

Solvent losses are often very great in a conventional or poorly maintained plant. In a poorly maintained plant, only about 20 percent of the purchased solvent quantity is generally recovered (Figure C-1).

Numerous solvent blends are used in the industry and accordingly, not all are equally recoverable. Table C-1 compares some CFC-113 based solvents for conventional recovery.

Depending on what measures have already been adopted at a facility, application of the guidelines summarized below can enable total emissions to be reduced by 90 percent. Solvent losses can be reduced from 2-5 $kg/h\text{-}m^2$ of bath area with conventional practice to 0.2 - 0.5 $kg/h\text{-}m^2$ of bath area. For certain alcohol based and partially aqueous systems, the overall base rate of annual losses is around 0.03 - 0.05 $kg/h,m^2$ of bath area (Ahmadzai, 1991a). The guidelines are concerned with the best available technology for the following:

- cold cleaning
- vapour cleaning (including equipment with spray/ultrasound)
- continuous "in-line" cleaning.

Table C-2 lists several VOCs and classifies them according to their importance in episodic ozone formation.

II. DESIGN OF THE CLEANING EQUIPMENT

1. Cover

For processes where:

- the solvent has a vapour pressure > 2 kPa (15 mm Hg) at 38°C (e.g., all halogenated solvents), or

- the solvent is heated, or

- the solvent is agitated mechanically, or

- where the equipment's opening is > 1.0 m^2,

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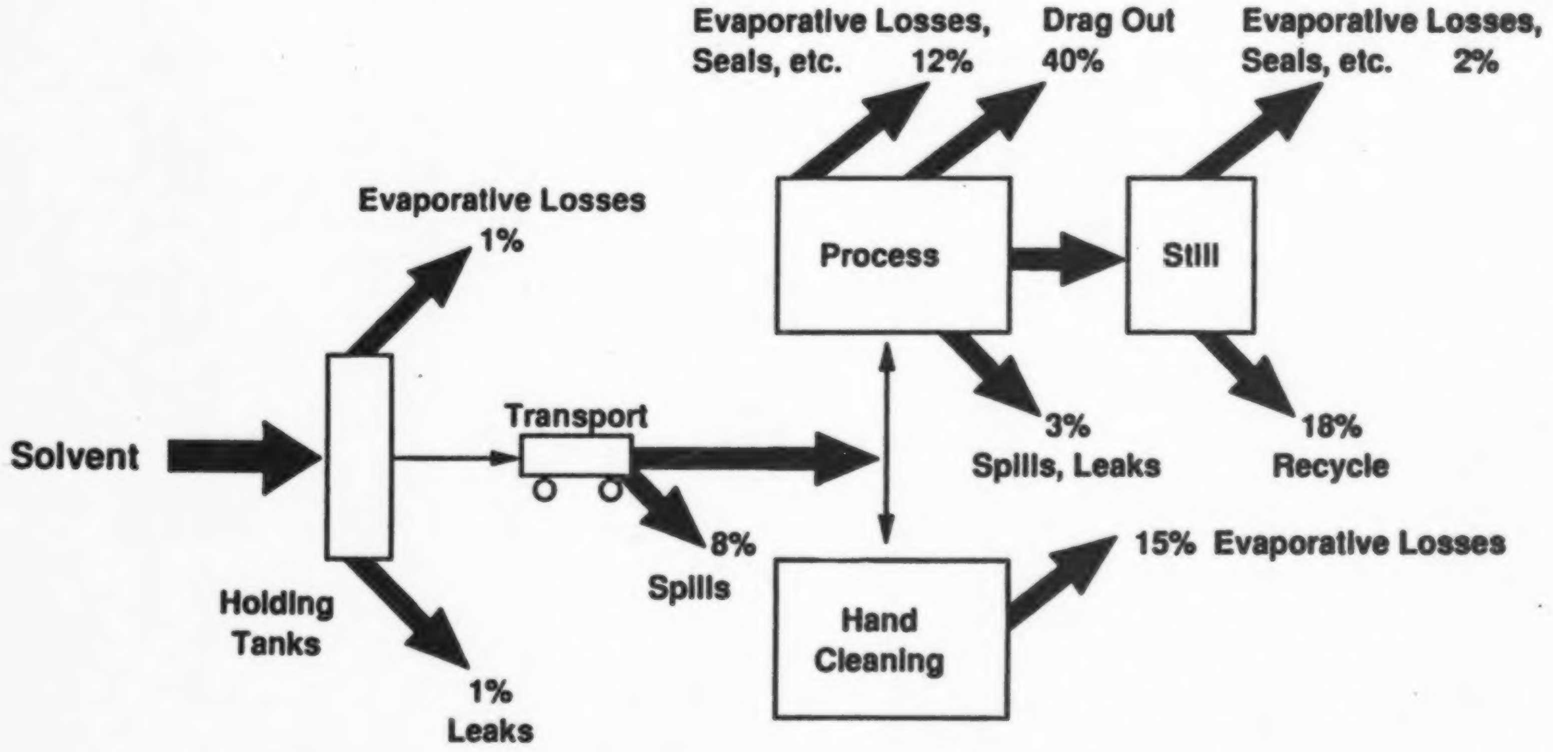
[1] The information presented in this appendix was provided by Dr. Husamuddin Ahmadzai.

Figure C-1

SOLVENT LOST IN A TYPICAL PLANT


Solvent
Holding
Tanks
Evaporative Losses
1%
1%
Leaks
Transport
8%
Spills
Evaporative Losses,
Seals, etc. 12%
Drag Out
40%
Process
3%
Spills, Leaks
Hand
Cleaning
15% Evaporative Losses
Still
Evaporative Losses,
Seals, etc. 2%
18%
Recycle

Source: Northern Telecom, 1989 CFC Program.

Table C-1. COMPARISON OF RECOVERABILITY BETWEEN CFC-113 SOLVENT GRADES

Grade	Major Use	Recoverability In-House (Yield)
Straight CFC-113	Vapour cleaning of plastic/ metals/glass	High
Azeotropes		
CFC-113/alcohols	Flux removal	High
CFC-113/acetone	Vapour cleaning of plastics	High
CFC-113/MC	Vapour cleaning of metals	High
Non-Azeotropes		
CFC-113/high bp alcohols	Flux removal	High
CFC-113/low bp alcohols	Flux removal	Low
CFC-113/water emulsions	Precision cleaning and drying	Low
CFC-113/displacement surfactants	Drying	High
CFC-113/lubricant	Metal working (e.g., riveting)	Zero

Source: Adapted from Clementson 1988c.

Table C-2. CLASSIFICATION OF VOCs

More important

Alkenes	
Aromatics	
Alkanes	> C6 alkanes except 2,3 dimethylpentane
Aldehydes	All aldehydes and benzaldehyde
Biogenics	Isoprene

Less important

Alkanes	C3 - C5 alkanes and 2,3 dimethylpentane
Ketones	Methyl ethyl ketone and methyl t-butyl ketone
Alcohols	Ethanol
Esters	All esters except methyl acetate

Least important

Alkanes	Methane and ethane
Alkynes	Acetylene
Aromatics	Benzene
Aldehydes	Benzaldehyde
Ketones	Acetone
Alcohols	Methanol
Esters	Methyl acetate
Chlorinated hydrocarbons	Methyl chloroform, Methylene chloride, Trichloroethylene and tetrachloroethylene

it should be possible to operate the cover automatically or with minimal effort. Cover design (e.g., horizontally sliding action) should permit operation that does not create turbulence in the vapour zone (e.g., avoid flip-open type design). The equipment should be designed so that the cover(s) opens and closes only during charging or discharging of the workload (e.g., air lock).

2. Arrangement for Drainage of Cleaned Components

For solvents with a vapour pressure > 2 kPa (at 30 mm Hg, 38°C), drainage should take place inside the machine with the cover closed.

3. Safety Devices

To prevent solvent evaporation during equipment stoppages, the following safety devices should be installed:

- Monitors and thermostats to check the flow of liquid to the condenser and heating element (< 18°C) and an equipment shut off in the event of a circulation stoppage or overheating.
- Spray monitor that shuts off the spray device if the vapour level drops 10 cm.

4. Operating Instructions Should be Posed Visibly and Should Summarize All Operating Steps

5. Design of Solvent Spray

To conserve solvent, the spray should be of the continuous type (not atomizing). The nozzle pressure should be regulated so it does not give rise to excessive splatter, and where applicable, be applied under the vapour level.

6. Design of Work Load Carrier

Components should be fed in automatically. The design of the work load carrier should facilitate drainage and not cause a "piston effect." A hook arrangement is preferable.

7. For solvents with a vapour pressure > 2 kPa (30 mm Hg, 38°C) or solvents that work at temperatures > 50°C, the following features should be incorporated where technically feasible:

- **Freeboard zone ratio**[2] should be 0.75 - 2.00, preferably ≥ 1.0 (ratio B/A in Figure A-2).
- **Water cover** (the solvent should not be water-soluble and should be heavier than water) should be ensured. Water

---

[2] The freeboard zone ratio is the ratio between the distance from the vapour level to the rim of the tank (the free-board height) and the width of the equipment.

cover counteracts evaporation of solvent (to the atmosphere).

- **Refrigeration coil** (mandatory with vapour cleaners) should have a working temperature of about -25°C. A defroster should be included. The following capacities can be adequate for this purpose:

Bath Width (m)	Cooling Capacity (Watts/m perimeter)
<1.0	190
>1.0	290
>1.8	385
>2.4	480
>3.0	580

- **Adsorption filter** shall be rated to ensure good function (at least 95% efficiency), so that outgoing solvent concentrations do not exceed 25 ppm[2] toward the end of an adsorption cycle. The ventilation air flow should be 15-20 m^3/minute and m^3 bath area.

- **Other technology** (e.g., thermal destruction) that can ensure a better or more efficient control of emissions than that described above.

Table C-3 depicts a comparison of some solvent recovery systems and Table C-4 summarizes available VOC control techniques, their efficiencies, and costs.

8. Design of devices for transport, filling and emptying of solvent.

Devices for transport, storage, and discharge of volatile solvents should be built as closed-loop systems.

III. OPERATION OF THE CLEANING EQUIPMENT

1. Prevent solvent losses from exceeding 10-20 WT percent of purchased quantity. Spent solvent should be transported and stored in closed vessels only.

2. Close the cover after each concluded work operation in the cleaning bath.

3. Place the components in a manner that permits complete drainage of solvent. The speed of component feed should not exceed 3 m/min vertically, 3-6 m/min horizontally. A slower feed speed is preferable (modern equipment permits horizontal speeds of 0.5 - 2.0 m/min and 0.3-0.8 m/min vertically). Hold in the vapour zone for at least 30 seconds or until condensation on the components

---

[3] Concentration in mg/m^3 = (molar weight in g>/22.414) (concentration in ppm). NOTE: 22.414 = molar volume expressed in litres at 0°C and 101.3 kPa.

Table C-3 COMPARISON OF SOLVENT RECOVERY SYSTEMS

TYPE OF SYSTEM	PRESSURE SWING ADSORPTION	FIXED BED	FLUIDIZED BED	LIQUID ABSORBENT
Adsorption or absorption	Activated carbon granule	Activated carbon granule or activated carbon fibre	Activated carbon bead	Fluorinated inert liquid
Desorption	Pressure swing (warm air)	Temperature swing (steam)	Temperature swing (hot air)	Temperature swing (distillation)
Liquefaction	Predemoisture cool under pressure	Cool	Cool	Cool
Water separation	Unnecessary	Necessary	Necessary in some cases	(Not clear)
Gas concentration	Applicable in a wide range	Applicable in a wide range	Inadequate for low concentration (needs preconcentration)	
Boiler	Unnecessary	Necessary	Necessary in some cases	
Blended solvents	Applicable	Not applicable	Applicable in some cases	(Not clear)
Treatment of wastewater	Unnecessary	Necessary	Unnecessary	Unnecessary

Source: Yamabe 1991.

Table C-4. A Summary of Available VOC Control Techniques, Their Efficiencies and Costs

Technique	Lower Concentration in Air Flow		Higher Concentration in Air Flow		Application
	Efficiency	Cost	Efficiency	Cost	
Thermal incineration **/	High	High	High	Medium	Wide, for high concentration flows
Catalytic incineration **/	High	Medium	Medium	Medium	More specialized for lower concentration flows
Adsorption */ (activated carbon filters)	High	High	Medium	Medium	Wide for low concentration flows
Absorption (waste gas washing)	-	-	High	Medium	Wide for high concentration flows
Condensation */	-	-	Medium	Low	Special cases of high concentration flows only
Biofiltration	Medium to high	Low	Low ***/	Low	Mainly in low concentration flows, including odour control

Concentration: Lower < 3 g/m^3 (in many cases < 1 g/m^3), Higher > 5 g/m^3

Efficiency:
High > 95%
Medium 80-95%
Low < 80%

Total cost:
High > 500 ECU/t VOC abated
Medium 150-500 ECU/t VOC abated
Low < 150 ECU/t VOC abated

*/ These processes can be combined with solvent recovery systems. Cost savings then ensue.

**/ Savings due to energy recovery are not included, these can reduce the costs considerably.

***/ With buffering filters to dampen emission peaks, medium to high efficiencies are achieved at medium to low costs.

ceases. Allow clean components to drain for at least 15 - 30 seconds or until they stop dripping. During vapour cleaning, components should drain until they are visibly dry.

4. Never clean porous materials (e.g., cloth, leather, rope) or absorbent materials in the vapour zone.

5. Keep the horizontal area of the workload to one-half the bath area.

6. Maintain between the workload and the edges of the opening at entry and exit a distance of < 10 cm or < 10% of the width of the opening (calculated on the basis of the workload silhouette).

7. Do not allow the vapour level to drop more than 10 cm when the workload is introduced into the vapour zone.

8. Never spray above the vapour level. Avoid spraying with cold solvent.

9. Check for leaks regularly throughout the entire system. The system includes cleaning and peripheral equipment (filters, storage, and filling/emptying devices, etc.). In the event of leakage, the equipment must be shut off and repaired immediately. A floor sump should be provided for collection of spillage.

10. Keep air flow ventilation below or at 15-20 $m^3/min,m^2$ of bath area unless a higher rate is required to meet mandatory work hygiene limits. Ventilation fans shall not be positioned near the bath opening.

11. Check to ensure that water is not visible in the solvent leaving the condensate separator (vapour cleaning system). Water forms a low-boiling azeotrope, increases solvent consumption, and causes corrosion damage. Water content should be maintained under 50-100 mg/l.

12. Shut off the equipment (vapour cleaning) if it is expected to remain idle for more than 2 hours.

13. Use a solvent filter to extend solvent life and reduce the amount of solvent waste. In general, solvent should be changed when the contamination level reaches about 10 percent by volume. Solvent should be added via closed-loop systems with entry below the liquid surface.

14. Check the acid acceptance of the solvent regularly, adjust as necessary. Typically, if acid acceptance values go below 0.08 weight percent as sodium hydroxide, monitoring should be frequent. Corrective action should be taken if the value reaches 0.04.

IV. WASTE TREATMENT AND DISPOSAL

Waste from degreasing processes are primarily hydrocarbons and solid residues and, depending on the pretreatment, can contain anywhere from 20 to 70 percent solvent and water condensate.

In some cases, single-plate distillation can be used to concentrate soils and recover solvent for reuse. Distillation combined with product filtration (e.g., ultra filtration) and desiccation can produce virgin quality solvent product assuming no other solvent may have been introduced as a contaminant. The oil can be concentrated for reuse.

Wastewater can be treated using activated carbon to remove trace solvent or can be sent to a waste disposal company for treatment. Still bottoms and unrecoverable solvent wastes can be disposed of by thermal destruction in commercial hazardous waste incineration or industrial furnaces equipped with appropriate scrubbing and particulate control technology.

Other treatment methods currently being researched are ozonation, hydrogen peroxide oxidation, carbon adsorption, and resin adsorption. These four processes may be used to treat wastewater generated during cleaning and degreasing operations by removing organics from the wastewater. Wastewater having undergone one or more of these processes successfully will have low enough concentrations of organics so that industrial wastewater treatment plants (IWTPs) can properly complete the regeneration of such water. The goal of using these treatments is to bring the final concentration of organics in wastewater below the regulatory agency's allowable limits.

Table C-5 illustrates emissions achievable with optimization of solvent-cleaning equipment. In addition, values of specific emissions occurring in the process of solvent cleaning are depicted in Table C-6.

Table C-5

TYPICAL EMISSIONS FROM OPTIMIZED SOLVENT CLEANING EQUIPMENT

Optimization 1	No. 2	Solvent 3	Losses Stand-by kg/h-m^2 4	0% load kg/h 5	100% load kg/h 6
Version 1	1	Chl-s*	0.12	0.3	0.7-0.8
Version 2	2	Chl-s*	0.02	0.05	0.35
	3	CFC-113	0.01	0.02	0.15-0.17
	4	Chl-s*	0.03	0.08	0.27-0.6
Version 3	5	Chl-s*	0.02	0.05	0.15
	6	Chl-s*	0.02	0.05	0.15-0.7
	7	Chl-s*	0.02	0.05	0.1-0.3
	8	Chl-s*	0.01	0.03	0.06

*Chl-s = Chlorinated solvent

Table C-6

VALUES OF SPECIFIC EMISSIONS OCCURRING DURING SOLVENT DEGREASING PROCESS (ECE TASK FORCE VOC)

SUBSTANCE	AMOUNT ($kg/h\text{-}m^2$)
Petrol	4.53
Kerosene	1.56
White spirit	5.80
Benzene	2.97
Trichloroethylene	3.94
Trichloroethane	4.20
CFC-113	14.91

APPENDIX D

CFC-113 AND 1,1,1-TRICHLOROETHANE CHEMICAL, TRADE, AND COMPANY NAMES

In order to maintain clarity in naming the solvents used in modern industry, chemical manufacturers and consumers have developed an "industry code" for naming chemical compounds. Compounds such as chlorofluorocarbons (CFCs) are followed by a three number code which identifies the composition of the compound. The code is defined as follows:

CFC-xyz

where:

x	is the number of carbon atoms in the compound minus 1 (if x=0, then it is omitted from the code);
y	is the number of hydrogen atoms in the compound plus 1; and,
z	is the number of fluorine atoms.

For example, the formula for trichlorotrifluoroethane is CCl_2FCClF_2. Applying the naming convention to the formula, the code becomes:

X = 2 - 1 = 1	No. of carbon atoms = 2
Y = 0 + 1 = 1	No. of hydrogen atoms = 0
Z = 3	No. of fluorine atoms = 3

Thus, the code is 113 (this compound is CFC-113).

There are currently ten manufacturers of CFC-113 in the U.S., Europe and Asia, plus an unknown number of manufacturers in the former Soviet Union, People's Republic of China, and Eastern Europe. As each has a different name for their product, Tables D-1 and D-2 list the product names, producers, and CFC content for CFC-113.

Different suppliers use Trade names in various ways: all of ICI's Arklone™ products are 113-based, the suffix referring to the composition, Arklone™ P and P-SM are pure 113, Arklone™ E, L, A, F, etc. are blended with other solvents, such as methylene chloride, isopropanol, ethanol, etc. However, Dupont's Freon™ products cover a wider range, including the refrigerants (for example Freon™ 11 and Freon™ 12). The Dupont 113-based systems have a prefix T (e.g. Freon™ TF, TMC, TP, TE, etc.).

1,1,1-Trichloroethane is also known by several other names. The most common of these alternatives is methyl chloroform. This name is often felt to be unacceptable because it implies that the product contains chloroform, which is not the case. Another name which is becoming more popular in the U.S. is "trike." The usefulness of this name is often discounted as well since this name has previously been used for trichloroethylene. Tables D-3 and D-4 list the producers of 1,1,1-trichloroethane, their Trade names, and the 1,1,1-trichloroethane content of the products.

TABLE D-1. CFC TRADE NAMES

Company	Country	Trade Name
ICI	UK	Arklone
Dupont	US	Freon
AtoChem	France	Flugene
Hoechst	Germany	Frigen
Kali Chem	Germany	Kaltron
ISC Chemicals	UK	Fluorisol
Allied	US	Genesolve
Montefluos	Italy	Delifrene
Asahi Glass	Japan	Fronsolve
Daikin	Japan	Daiflon
Central Glass	Japan	CG Triflon
Showa Denko	Japan	Flon Showa Solvent

TABLE D-2. CFC-113 CONTENT OF SELECTED PRODUCTS

Company	Product	% CFC-113
Dupont	Freon TMS	94.05
	Freon TES	95.2
	Freon SMT	69
	Freon MCA	62.8
	Freon TA	88.9
	Freon TDF	99.9
	Freon TWD 602	91.5
	Freon TP35	65
	Freon TE35	65
	Freon TMC	50.5
	Freon TF	100
	Freon PCA	100
Asahi Glass Co., Ltd.	Fronsolve	100
	Fronsolve AE	96
	Fronsolve AP	65
	Fronsolve AM	50.5
	Fronsolve AES	96
	Fronsolve AMS	94
	Fronsolve AD-7	99.5
	Fronsolve AD-9	99.5
	Fronsolve AD-17	83
	Fronsolve AD-19	82
	Fronsolve UF-1	80
	Fronsolve UF-4	86
	Fronsolve UF-5	90
	Fronsolve AC	87.5
	Fronsolve AW	97
	Nanofron E	96
	Nanofron A	75
	Nanofron B	65
Central Glass Co., Ltd.	CG Triflon	100
	CG Triflon E	96
	CG Triflon P	65
	CG Triflon M	50.5
	CG Triflon ES	95.5
	CG Triflon EE	92
	CG Triflon E35	65
	CG Triflon MES	93.3
	CG Triflon C1	98.7
	CG Triflon D1	99.5
	CG Triflon D3	99.4
	CG Triflon W1	91.2
	CG Triflon A	87.5
	CG Triflon FD	78
	CG Triflon CP	90
	CG Triflon EC	85.5

TABLE D-2. CFC-113 CONTENT OF SELECTED PRODUCTS (Continued)

Company	Product	% CFC-113
Daikin Industries, Ltd.	DAIFLON S3	100
	DAIFLON S3-E	96
	DAIFLON S3-P35	65
	DAIFLON S3-MC	50.5
	DAIFLON S3-ES	95.3
	DAIFLON S3-W6	91.5
	DAIFLON S3-EN	86
	DAIFLON S3-HN	90
	DAIFLON S3-A	87.5
	MAGICDRY MD-E6	94
	MAGICDRY MD-E35	65
	MAGICDRY MD 201	99.5
	MAGICDRY MD 202	99.5
	MAGICDRY MD 203	99.5
Du Pont-Mitsui Fluorochemicals Co., Ltd.	Freon TF	100
	Freon TE	95.5
	Freon T-P35	64.7
	Freon TMC	50.5
	Freon TES	95.2
	Freon T-E6	94
	Freon T-E35	65
	Freon T-DEC	93.5
	Freon T-DECR	64.5
	Freon TMS	94.0
	Freon SMT	69.1
	Freon T-B1	98.6
	Freon T-DA35	99.7
	Freon T-DA35X	99.6
	Freon T-DFC	99.9
	Freon T-DFCX	99.9
	Freon T-WD602	91.5
	Freon TA	88.9
	Freon MCA	63
ICI PLC	ARKLONE P	100
	ARKLONE PSM	100
	ARKLONE L	97.1
	ARKLONE AS	96
	ARKLONE AM	94.2
	ARKLONE K	75
	ARKLONE W	91.5
	ARKLONE EXT	64.7
	ARKLONE AMD	94.1

TABLE D-2. CFC-113 CONTENT OF SELECTED PRODUCTS (Continued)

Company	Product	% CFC-113
Showa Denko K. K.	Flon Showa FS-3	100
	Flon Showa FS-3E	96
	Flon Showa FS-3P	65
	Flon Showa FS-3M	50.5
	Flon Showa FS-3ES	96
	Flon Showa FS-3MS	50.5
	Flon Showa FS-3D	99.9
	Flon Showa FS-3W	91.5
	Flon Showa FS-3A	87.5

TABLE D-3. TRADE NAMES FOR 1,1,1-TRICHLOROETHANE

Manufacturer	Trade Name
ICI	Genklene Propaklone
Dow	Chlorothene* (R) Industrial Solvent Chlorothene* (R) NU Chlorothene* (R) SM Chlorothene* (R) VG Chlorothene* (R) XL Chlorothene* (R) SL Solvent Dowclene (R) EC-CS Dowclene* (R) LS [1]Dowclene* (R) EC Prelete* (R) Defluxer Solvent Proact* (R) Solvent [2]Aerothene* (R) TT Solvent Aerothene* (R) TA Solvent Film Cleaning Grade S.E.M.I. Grade [3]Methyl Chloroform, Low Stabilized - PW [3]Methyl Chloroform, Low Stabilized [3]Methyl Chloroform, Technical
AtoChem	Baltane
Solvay	Solvethane
PPG	Triethane
Vulcan	1,1,1, Tri
Asahi Glass	Asahitriethane
Toagosei	1,1,1, Tri
Kanto Denka Kogyo	Kanden Triethane
Central	1,1,1, Tri
Tosoh	Toyoclean

* Trademark of The Dow Chemical Company.

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[1] 75 percent 1,1,1-Trichloroethane and 25 percent perchloroethane.

[2] Aerosol Grade.

[3] Non-trademark product names.

TABLE D-4. 1,1,1-TRICHLOROETHANE CONTENT OF SELECTED PRODUCTS

Manufacturer	Trade Name	1,1,1-Trichloroethane Content %
Asahi Chemical Industry, Co., Ltd.	ETHANA NU	94
	ETHANA VG	94
	ETHANA AL	94
	ETHANA HT	94
	ETHANA RD	94
	ETHANA IRN	90
	ETHANA FXN	90
	ETHANA SL	94
	ETHANA TS	94
	ETHANA RS	84
	TAFCLEN (Dry cleaning solvent)	90
	AQUADRY 50	94
Asahi Glass Co., Ltd.	ASAHITRIETHANE	96
	ASAHITRIETHANE ALS	93
	ASAHITRIETHANE UT	96
	ASAHITRIETHANE LS	96
	ASAHITRIETHANE BS	92
	ASAHITRIETHANE V5	91
	ASAHITRIETHANE EC Grade	96
	SUNLOVELY (Dry Cleaning Solvent)	95
Central Glass Co., Ltd.	CG TRIETHANE N	97
	CG TRIETHANE NN	96
	CG TRIETHANE NNA	94
	CG TRIETHANE F	97
ICI PLC	GENKLENE LV	95.2
	GENKLENE N	95.4
	GENKLENE A	96.5
	GENKLENE P	99.7
	PROPAKLONE	89.6
	GENKLENE LVS	95.7
	GENKLENE LVX	90.7
	GENKLENE LVJ	95.2
	GENKLENE PT	99.9
Kanto Denka Kogyo Co., Ltd.	KANDEN TRIETHANE R	97
	KANDEN TRIETHANE H	97
	KANDEN TRIETHANE HA	94
	KANDEN TRIETHANE HAK	93
	KANDEN TRIETHANE E	98
	KANDEN TRIETHANE EP	97
	KANDEN TRIETHANE HB	94
	KANDEN TRIETHANE HC	94
	KANDEN TRIETHANE HF	94

TABLE D-4. 1,1,1-TRICHLOROETHANE CONTENT OF SELECTED PRODUCTS (Continued)

Manufacturer	Trade Name	1,1,1-Trichloroethane Content %
Kanto Denka Kogyo Co., Ltd. (continued)	KANDEN TRIETHANE HG	94
	KANDEN TRIETHANE HS	99
	KANDEN TRIETHANE HT	97
	KANDEN TRIETHANE N	100
	KANDEN TRIETHANE ND	97
	KANDEN TRIETHANE SR	90
	KANDEN TRIETHANE SRA	91
	KANDEN TRIETHANE EL	97
	KANDEN TRIETHANE ELV	97
Toagosei Chemical Industry Co., Ltd.	Three One-R	96
	Three One-S	95
	Three One-A	95
	Three One-AH	95
	Three One-S(M)	95
	Three One-F	95
	Three One-TH	95
	Three One-HS	95
	Three One-EX	90
	Shine Pearl (Dry Cleaning Solvent)	94
Tosoh Corporation	Toyoclean EE	97
	Toyoclean T	97
	Toyoclean SE	84
	Toyoclean O	100
	Toyoclean HS	96
	Toyoclean IC	91
	Toyoclean NH	96
	Toyoclean AL	95
	Toyoclean ALS	91
	Toyoclean EM	96

APPENDIX E

SITE VISITS

The following is a summary of the site visits conducted by committee members to aid in the preparation of the 1991 United Nations Environment Programme (UNEP) Solvents, Coatings, and Adhesives Technical Options Report.

Site Visit

IBM Jarfalla

The IBM Jarfalla plant was built in 1970 and specializes in building printers for all IBM markets. Control units for disk storage and bank terminal supports are also built at the plant which employs about 900 people.

This facility now has a strict environmental policy after having been self-admittedly one of the worst users of chlorofluorocarbons (CFCs) in Sweden, using 16 tonnes of CFC in 1986. They effectively now use no CFCs. They also have a complete control inventory of all chemicals under very strict regulation and an environmental policy which began in 1971.

IBM Jarfalla began an energetic program of elimination of CFCs by altering/changing the final steps of the initial sequence as well as changing the cutting oil. Stage I, which consisted mainly of "housekeeping" measures resulted in CFC use dropping to 4.7 tonnes in 1988, a 64% reduction. Stage II involved a CFC phase-out by either a cessation of oil use or a switch to oils which are water soluble or which form emulsions. In Stage III, the drying process was phased out. This was replaced by deionized (DI) water rinse with and without ultrasonics. The final stage is a dip in an inhibitor. Finally, a hot air dry is applied. All of these processes occur with no notable change in cleaning time.

The oily water is passed through an ultrafilter which costs 600.00 SEK. The total cost for CFC phase-out at Jarfalla was 300.00 SEK.

Site Visit

Siemens-Elema

Siemens-Elema specializes in the production of medical apparatus. Specifically, it specializes in medical applications such as X-ray technology, electromechanical devices (such as pacemakers), EKG equipment, and respirators, as well as dental and hearing aid devices. The firm employs about 2,000 people and is considered to be an extremely small CFC user. 1,1,1-Trichloroethane is used primarily to clean the pacemaker circuit boards. 1,1,1-Trichloroethane usage is estimated to be 4.2 Tonnes/year as a cold spray in an enclosed chamber.

The alternatives to CFC and 1,1,1-trichloroethane (TCA) cleaning are described below.

Alternatives to CFC as Cleaning Agents at Siemens-Elema

Electronic circuits for pacemakers:

Old Method		Present Method
Serial cleaning with Arklone F	'82-83	Spray cleaning with 1,1,1-Trichloroethane*
Vapour zone soldering Freon 113 as fluid	'89	IR-soldering

Other electronic equipment:

Old Method		Present Method
Semi-manual cleaning with perchloroethylene	'89	Rinsing with deionized water; hot air

* To be changed 92-93

Plans are to phase out CFCs and TCA with either isopropyl alcohol (IPA) or Ethanol sprays preferably by the end of 1991, but no later than 1993.

Site Visit

BALZERS AG

The Balzers Group is a division of Oerlikon-Buhrle, the latter employing 30,000 persons worldwide with sales of almost $3 billion. Balzers, with 3,900 employees and $300 M sales, are world leaders in high vacuum and thin film techniques. Both Balzers and Oerlikon-Buhrle are actively pursuing a CFC-113 policy, based initially on usage audits. Most usage within Balzers has already been eliminated.

Amongst their strictly defined product lines, Balzers also produces accessory equipment. This equipment includes aqueous cleaning machines for substrates and lenses prior to vacuum coating. A typical cleaner may clean ultrasonically about 500 ophthalmic lenses per hour. Drying was originally performed using alcohol followed by CFC-113. A demonstration was made of a modified machine which successfully dried the components by partially recirculating hot air. This machine will be marketed in the future.

Site Visit

Leica Heerbrugg AG

Leica Heerbrugg AG is a multinational organization which manufactures precision optical instruments, often with complex components. Total world sales reach approximately US$850 M.

Sensitive optical glasses have to be perfectly cleaned before coating. Leica Heerbrugg AG has adopted mixed aqueous/solvent techniques for cleaning. Previously, the final stages were in alcohol followed by CFC-113. Their active corporate environmental policy dictates as rapid a phase-out as possible and experiments have been made involving the following processes:

- drying in alcohol vapour
- drying in warm air
- drying by infra-red
- drying in warm air followed by evacuation
- drying in low pressure microwave plasma

None of these processes have shown a distinct lead over the others and all have considerable disadvantages. The Committee suggested that Leica might want to examine alcohol/perfluorocarbon drying as another approach, in the meantime taking care to limit CFC-113 emissions.

Site Visit

FFV Aerotech AB

FFV Aerotech is a member of the large industrial group Celsius Industries. The Celsius Group employs 13,000 people internationally and had 1991 sales projected at 9000 MSEK. The products manufactured focus on the marine, aviation, and electronics sectors. FFV Aerotech AB employs 970 people and markets maintenance and technical consultant services to the Swedish Defense Forces. It also develops advanced systems for the Swedish Air Force and carries out modification. The functions performed using ozone depleting solvents include the repair of airborne instruments and the development and manufacture of modifications. This FFV plant is one of the four industrial concerns in Sweden to receive an exemption (500 kg for 1991) to the phase-out of CFC-113. They have evaluated alternatives for their precision cleaning requirements and have approved a cleaning concept using ethanol and a KLN Ultraschell GmbH machine. Three of the machines will be in operation in mid-August and a fourth is in the process of procurement.

With the fourth machine, they will be completely free of the use of CFC-113 in their precision cleaning operation. The exemption granted them for the use of CFC-113 past January 1991, expires in August 1991. They are satisfied that the alcohol cleaning process they are installing will meet all Swedish requirements for explosion-proof, safe, clean effluent operation. One problem area that remains to be solved is the identification of a satisfactory solvent for removing a fluorinated grease of the "Krytox" type. For low temperature testing, the Company has successfully applied carbon dioxide impingement.

Site Visit

Plamex S.A.

Plamex S.A. manufactures telephone and other communication headsets. It is a subsidiary of Plantronics Inc., a company based in California, U.S.A. The company uses a CFC-113 blend to clean printed circuit boards. The facility consumes around 36 drums annually (1 drum contains 55 gallons of solvent). Of this amount, 6 drums of material is recovered and sent to a recycling facility. Each drum of virgin material costs about US$950.

After observing the operations, the committee members offered a number of suggestions on ways to reduce solvent use in the facility. These include the following:

- modification of vapour degreasers being currently used to replace lift lids with roll-back type lids; increased freeboard height, and a recommendation that the spray wand be used sparingly and properly;
- use of milder flux for rework to make it easier to clean;
- specification of solderability requirements of components before acquisition so as to minimize rework;
- careful storage of components in inert atmospheres so as to minimize any contamination; and
- rationalize the use of vapour degreasers in the facility so as to reduce the number.

Site Visit

Ensambles Magneticos, S.A.

Ensambles Magneticos, S.A. is a manufacturer of magnetic recording heads for rigid disc drives. It is a subsidiary of Sunward Technologies Inc., a firm with headquarters in California, U.S.A. The company uses CFC-113 for precision cleaning and defluxing of printed circuit board assemblies.

Ensambles engineers implemented a simple system that allows workers to slowly remove parts to reduce dragout. The technique uses a fixed rod mounted below the degreaser lid and a basket handle with hooks that allows the operator to raise the basket several inches at a time allowing the parts to drain.

The committee members gave a number of suggestions to the facility managers on ways to reduce the use of ozone-depleting substances (ODSs). These included the following:

- the use of an alcohol based wire cleaning solvent instead of CFC-113 based solvent. This would involve investigation of the type of drawing oils used in the manufacture of the wire and its solubility with alcohol
- change in the method of storing solvent drums to ensure minimal storage and handling loss; the working drum should be stored in a cool enclosed space
- improvement in the solvent transfer procedure from the drum to the degreaser. The use of manual or electric drill powered pumps to pump the material from the drum to the degreaser was recommended
- replacement of a lift lid with a roll-back type lid on the degreaser

Site Visit

Saab/Scandia

Saab Combitech Electronics produces electronics for each of the Saab/Scandia business groups and sells contract board assembly services to outside clients. They had 1990 sales of 1.9 billion with 204 MSEK profit. One-third of their solvent using production is for automobiles; one-third for space, automation, transportation control, and military; and one-third for contract assembly.

Their products range from simple, consumer grade products to sophisticated products for high reliability applications (automobile safety systems, missile control modules, space technology).

In 1986, one year prior to the Montreal Protocol, Saab made a corporate decision to reduce dependence on chemicals that deplete the ozone layer. Literally overnight, the electronics division was instructed to cancel plans to purchase new CFC vapour degreasers and to freeze annual use of CFC-113. This policy change occurred during a period of rapid sales increase.

Saab had been using a combination of in-line vapour degreasers, aqueous, and had cleaning processes. They used CFC-113 but no other chlorinated solvents because the federal environmental agency would not grant them a chlorinated solvent emission permit. The sequence of CFC elimination was:

1986	Corporate decision to freeze CFC use
1987	Vapour-phase CFC processes eliminated
1988	Carbon adsorption system installed
1989	Low-solid flux implemented
	Controlled atmosphere soldering machine purchased
1990	Controlled atmosphere/low solids implemented
1991	Process simplified; new flux investigations

Saab is now manufacturing without the use of CFC-113 or methyl chloroform solvents and is satisfied with the quality of its final products. They use Lonco 25 in a SEHO controlled atmosphere wave soldering machine; water soluble flux in an in-line aqueous/saponifier process; and alcohol cleaning (90% ethanol, 10% IPA) for rework and for touch-up prior to conformal coating (if used). Alcohol is also used for final cleaning of products for military customers. Boards are now cleaner than when they were using CFC-113.

The sequence of changes was more expensive than would be necessary today because the controlled atmosphere machine was an early generation model and there were difficulties of optimization resulting from oxygen contamination of the nitrogen supply and an inaccurate oxygen sensor. The investment costs are being repaid from savings in operating costs.

Site Visit

Atsugi Unisia Corporation

Atsugi-Unisia is a manufacturer of a wide range of car components including hydraulic tappets (valve lifters), pistons, clutch plates, 4-wheel steering systems, dampers, and air conditioning systems.

During 1990, their total use of ozone-depleting materials was:

CFC-12	96 tonnes
CFC-113	126 tonnes
1,1,1-Trichloroethane	864 tonnes

The CFC-12 was used for air conditioner compression testing. The CFC-113 was used for cleaning parts after machining and before heat treatment. 1,1,1-Trichloroethane was also used for this purpose and for electronics cleaning and had a very important use as a cleaner for pistons before the application of a PTFC/phenolic resin low friction coating. This is used as a long-life, low-friction coating on pistons for high performance turbo blown engines.

Atsugi plans to introduce aqueous alkali cleaning of the hydraulic valve lifter parts, and the piston precleaning and both aqueous cleaning and burn off degreasing for pre-heat treatment cleaning.

Currently aqueous cleaning of pistons is causing some loss of adhesion of the low friction coating and some adjustments to heat treatment will be required after both aqueous and burn off degreasing. The company plans to be out of CFC-113 and CFC-12 use by 1993 and out of 1,1,1-trichloroethane by 2000.

Site Visit

Minebea Group

Minebea Co. Ltd. heads a group of 52 subsidiaries and 14 affiliates with more than 25,000 employees and a sales turnover of almost Y230 billion.

The Company originated in 1951 as a maker of miniature ball bearings and is now the world leader in this field. The Company has pursued a course of expansion and diversification action, derived from both internal growth and strategic acquisitions. Precision technology and production expertise have been central to Minebea's development.

The visit was hosted by Mr. Mizugami, the Japan based Managing Director of Minebea. The plant at Bang-Pa-In, north of Bangkok, is the largest miniature precision bearing plant in the world.

The Group operation in Thailand comprises:

Pelmec Thai Ltd.
NMB Hi-Tec Bearings Ltd.
NMB Precision Balls Ltd. at Bang-Pa-In
Minebea Thai Ltd.
Thai Ferrite Ltd.
Taal Products (Thailand) Ltd. at Navanakoru
NMB Thai Ltd.
Minebea Thai Ltd. (Ayuthlaya Plant) at Ayuthlaya
Minebea Electronics (Thailand) Co. Ltd.
Minebea Thai Ltd. Lopburi Plant at Lopburi
Minebea Thai Agroindustry Co. Ltd. at Pathumthani

The company first came to Thailand in 1972 with a small plant manufacturing finished bearings from parts made in Japan. Currently they employ 17,000 people at Bang Pa-In and make 55 million pieces (i.e., finished bearings) per month.

Their current use of CFC-113 and 1,1,1-trichloroethane are:

CFC-113	90 tons per month
1,1,1-Trichloroethane	260 tons per month

Bearings are made from 440C (stainless) and 52100 carbon steel (corrodible). They also have a material similar to 440C, known as NMB alloy DD, which has quieter running characteristics.

They plan to phase out CFC-113 use by the end of 1995, and 1,1,1-trichloroethane use by the end of 1997.

The current method for cleaning bearing parts (rings, balls, retainers etc.) is:

1,1,1-Trichloroethane degrease
Detergent water clean
Wash in deionised water
Dewater in Freon TDFC

Rinse in Freon TF

The CFC-113 replacement process will be:

Water detergent clean
Water rinse
Dewatering oil

It should be emphasized that the cleaning process described above for bearing parts was demonstrated. However, this process cannot be used for assembled bearings because there is the possibility of chemical reactions occurring when dewatering oil is mixed with lubricant oil from bearings. Therefore, their main concern was to find a method for cleaning assembled bearings to remove particulate contamination.

Site Visit

ABB Automation

Circuit Pack Assembly:

Chronology			
Pre-1974	TH	Rosin Flux	Perchloroethylene clean
1974-1985	TH	WSF	Water clean
1985-1987	TH	WSF	Water clean
	SM	Rosin	CDC clean*
1987-1989	TH	WSF	Water clean
	SM	LSF	Water clean for solder balls**

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* ABB determined that they could not use WSF for SM due to component compatibility issues.

** Water is used to clean LSF soldered boards only for the purpose of avoiding ESD problems during brushing to remove solder balls. A dry brushing technique is desirable.

Policy Deployment:

- Local pressures from authorities and public
- Required elimination of 1,1,1-trichloroethane and methyl chloride by end of 1987 for PCB fabrication
- Permit denial for use of CFC for printed wire assembly (PWA) forced changes to occur
- Internal pricing of materials is used to force individual product lines to seek alternatives

Obstacles:

- Alkaline PC board processing has improved quality, but finer features will require improved technology

- LSF narrows process window, produces solders balls, causes crosses/icicles

Additional Information:

- ABB Automation was using a small amount of CFC-113 to clean artwork films. Changed over to alcohol (IPA) earlier in 1991.

- Produces 300,000 boards/yr (15,000-17,000 m^2/yr).

Site Visit

Siam Compressor Industry Co. Ltd.

This company is a joint Nippon-Thai venture, the main owners being Mitsubishi Electric Co. Ltd. and the Siam Cement Co. Ltd. The product line is exclusively small unit air-conditioner rolling piston type rotary compressors (approx. 2,250-11,000 kCal/h) which are used in equal parts for the domestic and export markets. The production capacity is 300,000 compressors per year.

The only solvent use is for cleaning diverse castings after machining. For this process, trichloroethylene is used in a conveyorized "hanging part" machine at 1 m/min. The key point is that the machine was constructed under license in Thailand to a Japanese custom design. As the parts being cleaned were soiled with, essentially, non-soluble and soluble cutting oils and grinding grit, with blind holes and intricate topography, ultrasonics were liberally applied in immersion tanks.

Internal distillation was sufficient to maintain adequate solvent purity as well as a vapour phase final rinse. The machine height was sufficient to ensure that the entry and exit slots were well over the freeboard.

Typical trichloroethylene (TCE) losses were very small, evidenced by the fact that the average measured exposure level is 2 ppm at any place. The average net and consumption must have been small with two 250 kg drums of new solvent used per month less the solvent content of three to four similar drums produced for solvent reclamation (percentage of solvent unspecified). Only new solvent was used. The used solvent was sent to a government reclamation facility.

Although not relevant to the solvents committee, a small quantity of HCFC-22 were used for Quality Control/Quality Analysis purposes. Currently this is all vented, but it is planned to reclaim it shortly, budgetary approval being currently in the process. Very tight wastewater control is also applied, an order of magnitude better than Thai regulations for suspended solids, dissolved metals and biological oxygen demand (BOD). The wastewater is used for irrigating the factory lawns. This example is evidence that tight environmental control is possible and economical in a developing nation and the Solvents, Coatings and Adhesives Committee and the Economics Committee were unanimous in congratulating SCI on keeping such an exemplary "tight ship".

Site Visit

Nissan - Japan

Nissan Motor Co. will phase out its use of CFC-113, -11, and -12 by the end of 1994, the fastest schedule for a motor company worldwide. By March, 1991, CFC-12 recovery and recycling equipment was installed in 3,000 Nissan service factories throughout Japan. By 1994, HFC-134a will be phased in as an alternative refrigerant for production models. CFC-11 blowing agent for foam has already been replaced with an air based foaming system. CFC-113 will be replaced with aqueous, semi-aqueous systems, and other alternatives by March, 1992.

Nissan Motor Co. cleans plastic car bumpers with methyl chloroform before painting. These uses will be replaced with an aqueous cleaning process.

Site Visit

AT&T - Thailand

AT&T has a consumer products factory in Bangkok, Thailand. It opened in Spring, 1990 CFC-free due to the upfront planning prior to opening. This factory, along with several other A&T operations, is furthering AT&T towards it's corporate goal to eliminate emissions of CFCs from manufacturing by the end of 1994.

Mr. Ken Lannin, Managing Director of the factory welcomed the committee and made opening remarks.

Dr. Stephen Andersen, the committee chairman, listed AT&T's leadership in environmentally-sound manufacturing including: aqueous cleaning work, terpene technology announcement in 1988, leadership in Ad Hoc Solvent Work Group CFC benchmarking and alternative testing since 1988, UNEP committee membership in 1989, International Cooperative for Ozone Layer Protection (ICOLP) inception in 1990, and United Nations Environment Programme (UNEP) committee membership in 1991. Dr. Andersen asked for AT&T's help in his proposed partnership between U.S. Environmental Protection Agency (EPA), Thai government, and Japan's Ministry of International Trade and Industry (MITI) which will work to eliminate CFC usage in Thailand.

Mr. Greg German, Director, Engineering, gave an overview of the factory in preparation for the tour. There are four assembly lines that make 10-12 corded telephone products. Low solids flux applied with AT&T spray fluxers is used to wave solder bare copper circuit boards coated with either a rosin-based or imidazole-based solderability preservative. By carefully selecting the right low solids flux and controlling the quantity with the patented AT&T-developed fluxer, post-solder cleaning is not necessary and therefore not done. The first generation AT&T spray fluxers are used in this factory. These, and second generation AT&T spray fluxers, have been implemented on many AT&T lines. Also, this technology is being offered commercially and has been implemented by other companies in the U.S.

The Moving Coil Receiver (MCR) line uses a hot-melt glue that does not contain 1,1,1-trichloroethane. Soldering is done manually with a low solids flux cored solder.

Plastic moulding is accomplished using a mould release compound with isopropyl alcohol (IPA), not CFCs.

Recycling in the factory is performed wherever possible including plastic, wood, paper, and moulding re-grind.

The director of purchasing and transportation, Visan Palattanavit, has started receiving surveys back from vendors regarding their CFC usage. To do this, he obviously has good knowledge of all suppliers. He stated that, other than IPA, very few chemicals are used.
(Guth)

Site Visit

Nissin Electric Co., Ltd.

Nissin Electric Company, Ltd. produces electrical substation equipment, reactive power compensation equipment, control systems, charged particle beam for semiconductor manufacturing, and engineering services to outside clients. The company had sales of 80,188 million Yen (US$507 million) in 1990 with a profit of 2,726 million yen (US$17 million).

Nissin has reduced its consumption of CFC-113 from 11 tons per year in 1986 to 4 tons in 1990. Over 40 percent of the 1990 consumption was used for defluxing of printed wiring assemblies (PWAs) as a result of the electronics soldering operation. The greatest part of the consumption (46.7 percent), was used for degreasing of oils from high vacuum equipment and 13.3 percent for degreasing of oils prior to thin film coating. The company has a goal of eliminating CFC-113 use by the end of 1995. Alternatives for replacing CFC-113 include the use of alkali washing processes to clean metal parts and the use of no-clean fluxes for PWA operations.

Nissin also consumes significant quantities of 1,1,1-trichloroethane. Reductions have been made from a 1986 high of 81 tons per year to 76 tons per year in 1990. The greatest use of 1,1,1-trichloroethane (55.8 percent) is in the degreasing of metal parts after machining operations and prior to chemical finishing processes. The next largest consumption of 1,1,1-trichloroethane (35.2 percent) is for dissolving of epoxy resin during cleaning/maintenance of equipment which mixes the resins for use in encapsulation processes as electrical insulating materials. Finally, 9 percent of the total 1,1,1-trichloroethane consumption is used for miscellaneous degreasing of other products. Alternatives for replacing 1,1,1-trichloroethane include alkali cleaning, isopropyl alcohol cleaning and the development of other alternative cleaning agents currently under development.

Although the minimization of 1,1,1-trichloroethane has been strongly pursued, a net decrease of 5 percent has been realized to date. Nissin feels that the elimination of 1,1,1-trichloroethane may be more difficult than CFC-113 because of the difficulty in finding a safe (worker exposure), nonflammable solvent with the solvency power for mixed epoxy resin that is provided by methyl chloroform. Nissin is also requiring their subcontractors to reduce and eliminate the use of CFC-113 and 1,1,1-trichloroethane on products supplied to Nissin.
(Felty)

Site Visit

Hitachi Construction Machinery Co., Ltd.

Hitachi Construction Machinery employs 4,500 people and manufactures a variety of construction machines including excavators, crawler cranes, shield machines, etc. Net sales were approximately US$ 1870 million in 1990.

In 1988, this plant consumed 15 metric tones of CFC-113. The consumption was reduced to 0.6 metric tonnes in 1990 by introduction of liquid petroleum gas (LPG) spray and water based cleaning. CFCs will be eliminated in 1995.

In 1990, 212 metric tons of 1,1,1-trichloroethane were consumed at this location. 1,1,1-Trichloroethane will be eliminated in 1998. Recent developments and observations aiding in the phaseout of these materials include the following:

- A water based alternative has already been introduced for components cleaning.
- 1,1,1-Trichloroethane is used as a cleaning agent in the process of heat treatment. Alternative technologies are now being investigated in several kinds of agents. These alternative technologies are rather difficult than those technologies currently being used.
- Operating costs of water-based cleaning is lower than previous solvent cleaning costs. But, operating costs for alternative cleaning in heat treatment processes is estimated to be higher than that of 1,1,1-trichloroethane.
- Waste water is separately treated in three systems for different kinds of wastes.

Site Visit

National Research Institute for Pollution and Resources - Japan

National Research Institute for Pollution and Resources is concerned with a wide range of research fields related to exploitation, processing and utilization of mineral resources and energy, mine and industrial safety and environmental protection. Research subjects include mineral resources development and utilization, energy development and utilization, environmental protection, and mine and industrial safety.

The visit to NRIPR at Tsukuba focused primarily on the research directed at the destruction of CFCs. Presentations were made on catalytic decomposition, recovery by adsorption, decomposition by thermal plasma, and thermal decomposition.

Catalytic decomposition is accomplished in a reactor at relatively low reaction temperatures of about 300°C using a fine powder catalyst. The catalyst basis is HY-Zeolite with TiO_2/ZrO_2. The residence time is 1-2 seconds and, at flow rates of 50 l/minute, is 100 percent efficient. The apparatus is laboratory scale. H-mordenite and TiO_2/ZrO_2 have the highest activity and selectivity.

Recovery by adsorption is based on adsorption on zeolite. Adsorption is effected by the zeolite pore size rather than chemical surface interaction. The process is based on size exclusion as the adsorption preference is in the order of CsY>KY>NaY where the large cation influences adsorption. Microwave radiation processes can be used for selective adsorption of CFC in water vapour.

CFC decomposition by thermal plasma reactor was achieved using a JEOL RF generator. Inductively coupled, radio frequency plasma reaction at 10,000°C using Argon gas were the conditions employed. The product distribution in CCl_3F decomposition by R.F. plasma was not encouraging where at least six different CFC decomposition products were identified.

Thermal decomposition of CFCs and industrial chlorinated organics studies were conducted in the presence of methane in which oxygen was in excess. The examination of thermal decomposition products revealed that the 99 percent destruction temperature (760°C) was almost the same with hexane as methane. The 99 percent destruction temperature for CFC-12 was 820°C.

Optimum conditions involving dilution with hydrocarbons and sufficiently high temperatures must be determined for complete incineration.

While these procedures operating at laboratory scale are encouraging in destruction efficiency and cost, the scale-up to industrial concentration destruction requirements needs to be explored on both an efficiency and costs basis. NRIPR researchers feel that "commercial" feasibility may take about 1-2 years and the strong candidate will be incineration.

Site Visit

Digital Equipment Corporation, Republic of Singapore

Digital Equipment Corporation is one of the world's largest suppliers of networked computer systems, software, and services. Digital leads the industry in open, multi-vendor systems integration. An international company, Digital does more than half of its business outside the United States, developing and manufacturing products and providing customer services in the Americas, Europe and the Pacific Rim.

The purpose of the visit was to observe the surface mount module manufacturing process which utilizes aqueous cleaning for removing process flux chemicals. The aqueous cleaner being utilized in Singapore is the High Performance Aqueous Microdroplet Module Cleaning system introduced by Digital Equipment Corp. in Washington, D.C. on April 5, 1990.

The Singapore plant converted from being a CFC user for cleaning surface mount products to an aqueous process during 1991. The plant tour exhibited how the system was being utilized, including showing its operational performance with the particular products being manufactured in the plant.

Questions by the participants ranged from defining the total installation time, understanding the energy usage of the equipment to the amount of CFC's eliminated by changing to an aqueous cleaning process. During the discussions it was mentioned that the advantages outweighed the disadvantages and the process is successful and is meeting all the manufacturing expectations. It was also demonstrated that aqueous cleaning is a viable reliable alternative, capable of successfully replacing CFC's as a cleaning methodology.

UNEP SOLVENTS COMMITTEE -- DUSSELDORF, GERMANY - 2 JULY 1991

Attending this meeting were several speakers and guests representing different associations and trade groups.

Dr. Heinrich Kraus	Ministry of the Environment (Speaker)
Dipl.-Ing. Christian Hering	Duerr (Speaker)
Mr. Peter Gunther	Machining-Association
Dipl.-Ing. Rupert Rompel	Environmental Affairs ZVEI (German Electric and Electronics Manufacturers Association)
Dipl.-Ing. Robert Auer von Brunkau	VCI
Dr. John Place	European Chemical Industry Federation
Dr. Hiemke	Environmental Ministry - Germany
Prof. Nader	VCI
Mr. G. Gabelmann	ITT Teves
Ing.-Dr. W. Schiegl	Siemens AG
Dr. Anne Janssen	Mannesmann
Mr. Karl-Heinz Pieper	Ministry of Finance
Mr. H. Schwenzer	IBM Germany

The meeting was hosted by the German representatives of the Solvents Adhesives and Coatings Committee, Gunter Gabelmann ITT - Teves, and Dr. Wolf-Eberhard Schiegl, Siemens.

Dr. Schiegl started the meeting off with a short description of the German situation, which is that they are faced with a phase out of ozone depleting solvents by the end of 1992 and they have a difficult job ahead of them. The industry was working with the Environmental ministry on a proposed date of 1993 when, at the last minute, the date was moved up to 1992 by the Burndersrat (Upper House). This will make things very difficult for German industry. Dr. Schiegl mentioned that it would be especially hard on the small printed circuit board manufacturers. Mr. Schiegl then introduced Dr. Kraus of the Ministry of Environment.

Dr. Kraus gave a very detailed review of the laws which are affecting the use of solvents and, in particular, those solvents that are ozone depleting substances. There are two different regulations facing Methyl Chloroform users in Germany; one is a prohibition on ozone depleting substances which was to go into effect on August 1, 1991, and the other is the revision of the Emission Control Act (2 BImSch V), in effect March 1, 1991.

Article 5 of the CFC Prohibition Ordinance deals with cleaning agents and solvents. This covers the manufacture of products and formulations containing ozone depleting substances to an extent greater than 1 percent by weight. There are exceptions to this part, such as use as a chemical cleaning agent in closed systems under 2 BImSch V, or to manufacture other less hazardous substances. The competent local (Laender) authorities may give temporary exemptions if the use is perceived to be absolutely necessary.

Article 2 of the Emission Control Ordinance (2 Bimsch V) limits volatile halogenated solvents for operating closed cleaning facilities to perchloroethylene, trichloroethylene, and dichloromethane, in a technical pure form.

CFC-113 and CFC-11 can be used until December 31, 1991 in already constructed facilities. By January 1, 1993, methyl chloroform will no longer be allowed unless by exemption.

2 Bimsch V defines the competent authority that may allow for exemptions as the Laender authorities, as well as the circumstances and individual requirements (such as economic hardship) for obtaining exemptions. The local authorities will have this authority.

The German regulatory action was thought by the Bundersrat to be necessary since so much TCA is used, and its "long" lifetime allows it to easily reach the stratosphere.

Dr. Anderson summarized Dr. Kraus' talk as follows:

Phase-out was reviewed as technically feasible by 1994, with special needs being met by exemptions. The implication is that Germany can accomplish this phase-out by 1992 with heroic efforts and can do it economically by 1994. Germany is a sophisticated, developed country, and as such, should be able to help other less developed countries; especially those dominated by multinationals such as South Korea and Singapore.

Dr. Anderson strongly urged that the German government and industry should contribute their experience to the on-going panel work and participate in the coming working meetings (August/September). Dr. Anderson mentioned the example of Mexico and their partnership program with the USA; they are ready to receive from the World Bank Fund and the Multi-Lateral funds to start the program.

Discussion of Dr. Kraus' presentation was as follows:

There was some concern that German industry, with this early phase-out date, might make an alternative choice that appears to be environmentally acceptable, then need to change again, thus undergoing the cost of the change twice.

Mr. Rumple pointed out that both the Environmental Ministry and Industry had been negotiating for a 1994 date, and were surprised at the last minute change to 1992.

Dr. Kraus is concerned that this law was passed too quickly and without enough deliberation and planning regarding the scope of its potential impacts. It would be possible to amend the law, but this would take two years, which is beyond the cut-off date.

Next, Mr. Gabelmann gave a description of the experience of ITT-Teves. Teves began to look at alternatives after the 1986 BiMSch laws were passed. Mr. Gabelmann traced the timeline for replacement of methyl chloroform in the ABS manufacturing system. It took from January 1987 until April 1991 to evaluate, test, select, install, start up, and de-bug the alternative system.

The ABS system involves a high priority for safety, multiple substrates and complex geometry.

Mr. Gabelmann pointed out the availability of parallel cleaning lines which allowed them the flexibility to be testing the new line without interfering with production; a luxury smaller companies will not have available. They estimated the cost to be 1.7 MM DM. A total of 12 cleaning lines need to be replaced in this one factory.

The problem areas they ran into were compatibility with other materials, adhesion of parts, and compatibility with other process, such as electroplating. There were problems with the equipment, such as chain drives, and electrical control filters. They also had new quality demands to deal with, such as new parts and materials to clean, that were not part of the original plans.

Small companies have special concerns, inadequate knowledge of the law, difficulty getting information, lack of trained employees, production demands on existing equipment which limits testing opportunity, and the unavailability of complete alternative systems.

Other issues that need to be addressed are the Water Act, and the requirements on waste water treatment plants. There is not enough experience in these areas to sufficiently handle all the requirements.

Dr. Schiegl then gave a summary of experiences of Siemens. He discussed a comparison of the environmental impacts of chlorinated solvents and aqueous cleaning.

Chlorinated	Aqueous
- Volume of water is small	- Water waste treatment
- Safe handling required tech. knowledge	- Batch treatment
	- Concentration by ultra filtration
- Sludge handling	- Sludge handling

He compared the operating costs for the solvent process with those for the new aqueous process in a printed circuit board operation.

	Actual	Normal
Maintenance	71	59
Electrical	8	12
Product	205	135
Waste Disposal	128	46
Total	412	252
DM/sq.m. of PCB	3.15	2.52

Mr. Herring of Duerr Equipment Company:

Mr. Herring summarized the availability of equipment that will use the solvents that are allowed under the new emission laws with their very tight limits. First, he discussed the availability of very tight degreasers that will use solvents, allowed under the new emission limits. He explained how the equipment works and minimizes any emissions to the environment and protects the worker from exposure to the solvent vapours. Since 1985, they have sold 500 degreaser units.

Mr. Herring also detailed the aqueous equipment which his company makes, 50 of which have been sold since 1988. Today, 75 percent of the cleaner machines he makes are aqueous and 25 percent are solvent-based.

Mr. Herring said that it was not possible to replace all the equipment in two years. He does not think hydrocarbons are ready yet and there is currently no hydrocarbon equipment. It takes approximately one year to deliver the equipment after the order is received.

A discussion period followed the presentations.

Prof. Nader pointed out that the German law did not undergo any technical review, and was a political action. German companies will have to deal with the two laws, the CFC/Halon regulation and the 2 BImSch V regulation. Industry will either need to seek local exemptions under these laws, or use the materials allowed under the BiMSch requirements (i.e., using other chlorinated solvents with extremely low emission levels).

Other alternatives that the German industry can use are to search for and implement alternative materials, although the short time frame will not allow for much of this. Importation of products containing or manufactured with ozone depleting substances is not restricted in any way so that adhesives and glues can be formulated outside of Germany, then imported for use in Germany. Also, manufacturers can have parts shipped out of the country for processing such as cleaning and then shipped back for installation.

Summary comments.

Steve Anderson - Chairman Solvents Committee: Equipment manufacturers need to work hard to make the changes in Germany. They should expand manufacturing capability to meet the short term needs of the German situation, then be positioned to help the rest of the world. The German industry should organize into expert teams and make their expertise available to the rest of the world after they complete the German phase-out.

Dr. Schiegl: A 1994 phase-out would have been hard to meet, but industry would have pushed hard to meet it. The 1992 date is out of range since it will take about five years to make the required changes. Germany is further ahead than most countries because they have had, for some years, aggressive regulations on solvents and companies have programs in place to try to eliminate their use.

Mr. Gabelmann: Four to five years is needed to convert a challenging and difficult application. Smaller companies are not sure if they can meet even that schedule. German industry may need to send products to foreign countries and will need to seek exemptions under local regulations.

Mr. Romple: A lot of information needs to get out to the smaller companies. They need time to think about and react to the regulations. What will happen at this time is unknown.

EEC laws give standard requirements for the community and member countries and can be very stringent on environmental matters. Sweden, although not a member of the EEC, did not have an equipment shortage during their phase, but the product split in Sweden is different to Germany and other European countries. Trichloroethylene dominates the metal cleaning sector with 1,1,1-trichloroethane having a very small share, due mainly to the strong position of the indigenous trichloroethylene producer. Ninety percent of telecommunications allowed for relatively easy substitutions by "no clean" fluxes. In Germany, much of the CFC-113 in use is for precision and mechanical cleaning which is more difficult to substitute.

General summary comments of the session:

- Adhesives and fine line space circuit boards and other specialized uses will be problem areas.
- Aggressive German phase out will shift some production to other countries and/or lead to exemptions.
- Notification of the large numbers of users is critical, information on know-how and engineering is needed for smaller users.
- There may be a shortage of experts to deal with the problems.
- There may be a shortage of supply in new equipment. Dr. Anderson expressed confidence that equipment supplies will be able to meet the challenge.

Evening Session:

A brief special evening meeting was held to accommodate a last minute request of the Japan Alcohol Association. This association has been conducting tests for the comparison of cleaning with ethanol and ethanol/water mixtures as alternatives to CFC cleaning. The special delegation was represented by association members, producers, and an equipment supplier. They presented preliminary data showing effective cleaning using alcohols, chiefly ethanol. The study so far indicates that alcohols and blends are effective cleaners; one must have the proper equipment and deal with water contamination. They have additional work underway to help further define their process and applications areas.

APPENDIX F

SUMMARY OF TESTING PROGRAMS FOR ALTERNATIVES IN THE ELECTRONICS INDUSTRY IN SWEDEN, UNITED KINGDOM, AND THE UNITED STATES

TABLE F-1. COMPARISON OF US, UK, AND TRE INTERNORDIC CLEANING OPTIONS EVALUATION PROGRAMMES

Collaboration Timescale Monitor	IPC/DOD/EPA	UK	UK	TRE Internordic
	Voluntary 1988-1992/3 IPC, etc.	Contractual 1990-1992 DTI/MOD	Contractual 1990-91 NPL	Contractual 1988-92 IVF Sweden
TEST VEHICLE				
Substrate	FR4	SMT : FR4 Mixed Tech : FR4 SMT : Ceramic	FR4	FR4
Components	LCC	PLCC; QFP; SOIC chip capacitors	QFP; PLCC	LCC, PLCC, DIL, SOT, chip capacitor
Max I/O	68	160	100	68
Min Pitch	0.050"	0.025"	0.025"	0.025"
Min Stand-off Height	0.005" (fixed)	-	0.003"	≈ 0.003"
Flux	RA	RA; RMA; No clean	RMA; Water soluble	RMA, No clean, OA
Soldering Method	VPS; Wave	IR; Wave	IR; Wave	VPS, IR, Wave
ASSEMBLY	Multi-site Multi-line	Central Single Line	Multi-site Single Line	Multi-site
CLEANING OPTIONS DATA				
CFC	(1989) Phase 1	1992	1990	Complete
Semi-Aqueous	(1991) Phase 2	1992	1990	Complete
HCFC	(1991) Phase 2	1992	1990	-
Aqueous	(1993) Phase 3	1992	1990	-
Low Solids Flux	(1993) Phase 3	1992	1991	Complete
Cont. Atmosphere	(1993) Phase 3	1992	-	Complete
Alcohol	-	1992	1990	Complete
				1992: Off-shelf commercial products, water cleaning micro-emulsion storage, handling, white residues

APPENDIX G

LIST OF MEMBERS OF ICOLP AND JICOP

INTERNATIONAL COOPERATIVE FOR OZONE LAYER PROTECTION MEMBERS LIST OF ICOLP

AT&T

British Aerospace

Ford Motor Company

Hitachi Limited

Honeywell

IBM Corporation

Mitsubishi Electric Corporation

Motorola Corporation

Ontario Hydro

Northern Telecom

Texas Instruments

Toshiba Corporation

MEMBER'S LIST OF JICOP

(as of Sept 1994, in alphabetical order)

Aerosol Industry Association of Japan

All Japan Laundry and Drycleaning Association

Association of Methyl Bromide Industry Japan

Association of Polyurethane Foam Industry

Chemicals Inspection & Testing Institute, Japan

Communications Industry Association of Japan

Electronic Industries Association of Japan (EIAJ)

Electronic Materials Manufacturers Association of Japan

Extruded Polystyrene Foam Industry Association

The Federation of Electric Power Companies

Federation of Electroplating Industry Association, Japan

The Federation of Pharmaceutical Manufacturers' Associations of Japan

The Glass Manufacturers Association of Japan

Heat Treatment Trade Association of Japan

High Expanded Polyethylene Foam Industry Association

Industrial Pollution Control Association Japan

Japan Adhesive Industry Association

Japan Air Soft Gun Association

Japan Alcohol Association (JAA)

Japan Aluminium Federation

Japan Association for Hygiene of Chlorinated Solvents (JAHCS)

Japan Association of Refrigeration & Air-Conditioning Contractors

Japan Association of Wholesales for Laundry and Drycleaning

Japan Auto Parts Industries Association (JAPIA)

Japan Automobile Manufacturers Association, Inc. (JAMA)

Japan Automobile Service Promotion Association (JASPA)

The Japan Bearing Industrial Association (JBIA)

Japan Business Machine Makers Association (JBMA)

Japan Camera Industry Association

Japan Chemical Importer's Association (JCIA)

Japan Chemical Industry Association

Japan Chemical Industry Ecology-Toxicology & Information Center (JETOC)

Japan Clock & Watch Association (JCWA)

Japan Container Association

Japan Cosmetic Industry Association

Japan Dyestuff & Chemical Industry Association

Japan Electric Measuring Instruments Manufacturers' Association (JEMIMA)

The Japan Electrical Manufacturers' Association (JEMA)

Japan Electronic Industry Development Association (JEIDA)

The Japan Fire Extinguishing System Manufacturers' Association

Japan Flon Gas Association

Japan Industrial Conference on Cleaning (JICC)

Japan Information Service Industry Association (JISA)

The Japan Iron and Steel Federation (JISF)

Japan Laundry and Drycleaning Conference (JLDC)

Japan Metal Sash Institute

Japan Metal Siding Industry Association

Japan Metal Stamping Association

Japan Petrochemical Industry Association (JPCA)

Japan Prefabricated Freezer and Refrigerator Industrial Association

Japan Printed Circuit Association

The Japan Refrigeration and Air Conditioning Industry Association (JRAIA)

Japan Semiconductor Parts Industrial Association

Japan Soap and Detergent Association

The Japan Society of Industrial Machinery Manufacturers (JSIM)

Japan Surfactant Industry Association

The Japan Valve Manufacturers' Association

Japan Wood Preservers Industry Association (JWPIA)

Japanese Association of Refrigeration

Japanese Consumers' Co-Operative union (JCCU)

The Japanese Electric Wire & Cable Makers' Association

National Federation of Petroleum Commercial Association

Research Institute of Innovative Technology for the Earth, Department for the New Generation Refrigerant Research

The Society of Japanese Aerospace Co., Inc.

Ultrasonic Manufacturers Association

APPENDIX H

ANALYSIS OF CURRENT AND FUTURE PRODUCTION OF CARBON TETRACHLORIDE

(Reproduced from the 1994 Report of the UNEP Aerosols, Sterilants,
Miscellaneous Uses, and Carbon Tetrachloride Technical Options Committee)

VI. CARBON TETRACHLORIDE (CTC)

6.1 Introduction

Carbon tetrachloride (CTC) is a heavy, colourless liquid at normal temperatures and pressures (boiling point 77°C). It is non flammable, miscible with most organic liquids and is a powerful solvent. In the past CTC has been used for charging fire extinguishers, as grain insecticide fumigants, as an antihelminthic agent (especially for the treatment of liver fluke in sheep) as a solvent in the rubber industry and most commonly as a dry cleaning solvent and metal degreasing solvent. It has been almost completely supplanted in the developed countries by less toxic and often more effective materials for all these uses but it is believed to still be used, for example as a grain fumigant in some developing countries.

CTC is the most toxic of the chloromethanes (10 ppm by volume in air threshold limit as a maximum safe concentration for daily 8hr exposure [26]). It is harmful if swallowed, inhaled or absorbed through the skin and its vapour decomposes on contact with flame or very hot surfaces to give off phosgene and other toxic products. CTC vapour or mist is irritating to the skin, eyes, mucous membranes and upper respiratory tract. Exposure can cause stomach pains, vomiting, diarrhoea, nausea, dizziness and headaches, and damage to the eyes, liver and kidneys.

CTC is produced primarily as a feedstock for CFC 11/12 production in which it is converted to the respective CFC by replacement of either one or two chlorine atoms by fluorine atoms, normally in a process where CTC is reacted with hydrogen fluoride (HF) in the presence of a catalyst.

There are a number of other minor feedstock uses of CTC, in which the CTC is entirely transformed during the process, which are permitted under the Montreal Protocol. These feedstock uses include the production of key pharmaceutical and agricultural chemicals and use as a catalyst promoter in oil refineries.

It is important to distinguish between dispersive and non-dispersive uses of CTC. There are a number of possible ways of interpreting what is and what is not a dispersive use of CTC (and other controlled substances). For the purposes of this report the following definitions have been applied:

> A dispersive use is any use of CTC in which all or some part of the CTC is emitted to the environment, for example laboratory use (eg. spectroscopy), inert reaction solvent (eg. pharmaceutical manufacture).
>
> A non-dispersive use is any use in which the CTC takes part in the reaction and is, thereby transformed into another chemical, for example CFC manufacture, catalyst reforming, reagent use.

There is a grey area where the CTC may react partially in the process. This is claimed to occur during the manufacture of chlorinated rubber.

A very small percentage of CTC production is used for dispersive uses. The main dispersive use is as a solvent for materials undergoing chlorination, the majority being used in the production of chlorinated rubber and small quantities are used as a process solvent in the pharmaceutical industry. In certain circumstances, it is possible to make such uses virtually non-dispersive by the application of modern technology and thermal oxidation processes.

A small but important dispersive use of CTC is the laboratory use of CTC for example, a solvent for infra-red analysis of oil. Dispersive uses are described in more detail below.

Inadvertent production of CTC also arises in some important industrial processes. For example, in the production of chlorinated solvents, chloromethane and vinyl chloride. In most cases the CTC is either recycled and destroyed within the production unit or is used as a feedstock for production of another chlorinated derivative. For example, CTC produced in vinyl chloride monomer plants is often used as a feedstock in the production of either trichloro- or tetrachloroethylene. Alternatively, CTC may be thermally oxidised to produce either hydrogen chloride(HCl) or chlorine which is then recycled for use in chlorination or oxychlorination processes. Small trace levels of CTC will remain in the final chlorinated derivative. It is estimated that these levels do not exceed 100 ppm and are generally 10 ppm. This issue is under review by the United Nations Environment Program (UNEP) Technology and Economic Assessment Panel.

6.2 CTC Production and Consumption

CTC is normally produced by the high temperature chlorination of propylene or methanes, usually known as chlorinolysis. Other starting materials include vinyl chloride (VC) by-products, ethylene dichloride, propylene dichloride, chloromethane by-products and propylene oxide by-products. CTC can also be produced by chlorination of carbon disulphide. Production facilities for CTC usually produce CTC alone or CTC and perchlorethylene as joint products - these latter facilities can usually be tuned to produce either 100% perchlorethylene or 100% CTC by recycling within the plant.

The global production data for CTC has not been reported. It is anticipated the data collected under the Montreal Protocol will provide information on production for non-feedstock uses and consumption in the future. It is possible to estimate total CTC production for CFC production by using the following formula:

CFC 11 produced x 1.14* = CTC consumed

CFC 12 produced x 1.30* = CTC consumed

((*): These figures are average values and for guidance only)

By using data provided by the Alternative Environmental Acceptability Study (AFEAS) [Production, Sales and Atmospheric Release of Fluorocarbons through 1992, Alternative Fluorocarbons Environmental Acceptability Study 1993 [3], it is possible to make the following estimates (in tonnes).

Year	CFC 11	CTC*	CFC 12	CTC*	Total CTC
1990	232,916	265,524	230,950	300,235	565,759
1991	213,486	243,374	224,805	292,247	535,621
1992	186,373	212,465	216,262	281,141	493,606

AFEAS estimate that between 18-31% of 1991 production of CFC 11/12 is unreported in the above data. Data are not included in the above Table for the following countries, Argentina (in part), States of the former Commonwealth of Independent States, the Czech Republic, the Slovak Republic, India, China, Romania and South Korea.

The most comprehensive data worldwide on CTC production and consumption is that published by the Japanese Association for the Hygiene of Chlorinated Solvents (JAHCS). These are summarised below.

Production and Consumption of CTC in Japan (tonnes)

Year	1988	1989	1990	1991	1992
Production	60,790	57,530	52,039	51,475	49,539
Import	47,996	44,219	19,868	17,013	2,481
Export	16	37	516	2,200	2,648
Consumption	108,770	101,712	71,391	66,288	49,372
CFC Feedstock	101,692	93,135	63,305	58,595	44,449
Miscellaneous	7,078	8,577	8,086	7,693	4,239

Miscellaneous uses described in the Table include other feedstock uses of CTC. Miscellaneous Use of CTC in Japan is estimated to be about 6000 tonnes. Dispersive uses in Japan in 1989 was approximately 7600 tonnes. The largest portion of this volume was consumed by the chlorination of rubber and poly-olefin which accounted for some 3000 tonnes in 1989. Producers are still working on a feasible substitute with phase out of CTC expected by the end of 1994.

Inadvertent CTC production is not reported. This topic is dealt with separately by the Technology and Economic Assessment Panel. It is anticipated that this material will continue to be produced. The majority will be recycled or destroyed with small quantities being isolated and purified to be used as feedstocks for other chlorinated hydrocarbon processes or as feedstock for the production of pharmaceuticals and agrochemicals, as permitted under the Protocol.

6.3 Non-Dispersive Uses of CTC

The main use of CTC is as a feedstock for CFC 11 and 12 production. It can be estimated that 95 to 97% of CTC production is used in this manner. Reported world wide production [3] of CFC 11 and 12 has declined from 748,511 metric tonnes in 1986 to 402,635 in 1992 with a corresponding decline in CTC production. This will decline further as CFC phase out is approached.

It is possible to hydrogenate CTC to chloroform and this may become a way of disposing of involuntary CTC production. No operating full-scale processes are known.

CTC is also used as a feedstock in the manufacture of a number of important fine chemicals, agrochemicals and pharmaceuticals. Products manufactured include the pesticides chloranthil, DCPA, picloram, permethrin and cypermethrin, the drugs AZT and dalacin and the production of the important intermediate trityl chloride.

CTC is used as a 'catalyst sweetener' in the petrochemical industry where its role is to maintain the presence of chloride ions on the catalyst surface. The CTC is destroyed within this process but it is likely that non-ozone depleting substances such as tetrachloroethylene or ethylene dichloride could be, and are used to provide this a similar effect.

Another small volume application is in the stabilisation of liquid sulphur trioxide for transport and storage. It is claimed that the CTC reacts with the SO_3 in situ to form the stabilising agent as shown in the reaction below:

$$2SO_3 + CCl_4 \text{ -------->} \quad COCl_2 + S_2O_5Cl_5$$

Reagent

CTC is an important reagent in several reactions. When used as a reagent CTC is consumed or chemically altered so this can be considered a non dispersive use.

Supercritical CTC reacts with metals such as niobium and tantalum to form chloride salts. This reaction can be used to purify the valuable metals from their oxides.

CTC is used in free radical reactions and will add across double bonds to functionalise olefins [27]. For example, CTC adds across the double bond in ethyl vinyl ether to give the functionalised ether.

Alcohols can be converted into chlorides using triphenyl phosphine and CTC under mild conditions [28]. A similar procedure can be used to open epoxides to give *cis*-vicinal dichlorides [29], and to chlorinate enolisable ketones and ureas [30]. In general there are many other chlorinating agents for these purposes but in some cases this reaction cannot be substituted.

Aldehydes, ketones and some esters react with CTC in the presence of triphenylphosphine, tris(dimethylamino)phosphine, and other reagents, to give the dichloromethylene derivative [31]. CTC is often used as the solvent as well as the reagent in this reaction.

The radical degradative chlorination of carboxylic acids and acid chlorides using CTC and 2 - mercaptopyridine - N - oxide has been used to prepare, otherwise difficult chloro compounds from the corresponding carboxylic acids [32].

Other useful reactions using CTC as a reagent include its use as a trichloromethylating agent in Friedel-Crafts type reactions [33] and as a chlorine source in the palladium catalysed chlorination of trialkylsilanes to give trialkylsilyl chlorides [34].

In all cases, at the research level, the world consumption of CTC as a reagent is very small compared with other uses.

6.4 Dispersive Uses of CTC

CTC is classified by most regulatory authorities as a 'possible' human carcinogen, and as such its use in dispersive applications is small in countries with strict occupational health and safety legislation. These regulations require that most applications of CTC are totally enclosed with recovery and recycling equipment.

6.4.1 Chlorination Reactions

The largest use of CTC outside CFC production is as an inert solvent in chlorination reactions. Other non-ozone depleting chlorocarbons are not suitable for this application as they are either not inert or do not have the required solvency properties. Indeed, in some cases, for example the manufacture of chlorinated rubber, there is evidence that CTC plays an essential role as a reagent in chlorination reactions with a small percentage reacting, and thereby being destroyed in the process. Considerable work is being carried out to identify alternatives , and in a number of cases to minimise CTC emissions. In general, CTC is recycled and losses are low. The average recovery efficiency is about 98%. In new plants recovery rates exceeding 99.9% can be realised. With modern technology and the incineration of CTC containing process residues, it is possible to reduce emissions to a practicable minimum. In such circumstances such applications could be considered as 'non-dispersive' and with appropriate monitoring could be permitted to be continued after the CTC phase-out.

The major products where CTC is used as a solvent are chlorinated ethylene vinyl acetate copolymers, chlorinated polyethylene and chlorinated polypropylene, which are used principally in marine and weatherproof paints (EEC use of CTC in chlorinated rubber manufacture in 1989 was approximately 2300 tonnes, but is anticipated will have reduced significantly since 1989).
There is a trend away from chlorinated rubber paints with aqueous and other polymer based systems becoming available although for some applications it is extremely difficult to find alternatives as no other paint system offers all the superior properties which are combined in chlorinated rubber. In many countries, specifications and standards demand the use of chlorinated rubber systems which have been subjected to rigorous and long term testing procedures to guarantee their efficacy in use.

In these areas the alternatives will have to be subjected to similar testing regimes prior to their adoption. By the end of 1995, Japanese chlorinated rubber producers will have moved to alternatives.

CTC is used as an inert solvent in chlorination reactions for the manufacture of a number of pharmaceutical products or intermediates, such as the drug, Ibuprofen. In certain circumstances other inert solvents such as chlorobenzenes may be appropriate but these will require pharmaceutical approval which can take up to 5 years.

It is believed that CTC is still used as a cleaning solvent in parts of Eastern Europe, India, South East Asia and USSR and this view is supported by measurements of atmospheric CTC concentrations. However, no data on CTC use in this region have been obtained.

Another application is the use of CTC in the palm oil industry in South East Asia as an extractant. Consumption data are not available.

6.4.2 Laboratory Uses

The unique physical and chemical characteristics of CTC have led to its adoption worldwide as a laboratory solvent for many different applications. CTC is used for routine chemical analysis for the operation and environmental control of many chemical manufacturing plants. It is also used for the research and development of technologies and products in most laboratories throughout the developed and developing world. As a result of its unique characteristics there are few alternatives which are available.

Some examples of CTC laboratory use include:

- extraction solvent
- reaction solvent
- eluent for chromatography
- spectroscopy
- analysis standard

Current consumption rate worldwide is estimated to be less than 1000 tonnes per annum. The majority of analytical methods using CTC are documented standards which will require changing through individual national and international standards organisations.

CTC used for laboratory uses is distributed to laboratories worldwide through a totally different route than the majority of applications discussed in this chapter.

In most circumstances it is marketed as ultra pure grade or as spectroscopic standards in containers which vary in volume from a few hundred millilitres to a size of five litres. In most analytical techniques only a few millilitres is used per analysis.

Extraction Solvent

CTC is a powerful non polar solvent for many organic compounds and its use is specified in many national and international standard procedures. With the range of solvents available for extractions, its use for this purpose could cease immediately in the majority of cases with little disruption to normal laboratory procedure, were it not for these standards. Because of the known toxicity of CTC it is generally used as an extraction solvent only as a last resort.

One example of the use of CTC as an extraction solvent used in an analysis standard is the Wijs method for determining the "iodine value", a common parameter measured in edible oils. The test involves dissolving the oil or fat in CTC, adding standardised Wijs solution, then after the reaction is complete adding potassium iodide solution and titrating the free iodine with sodium thiosulphate. CTC is used as the solvent because it is inert to Wijs solution. Alternative methods to the Wijs procedure will need to be developed in order to cease this dispersive use of CTC.

Inert Reaction Solvent

CTC is used as a inert reaction solvent in several useful chemical procedures. Regioselective bromination reactions using *N*-bromosuccinimide (NBS) and regioselective chlorinations using *N*-chlorosuccinimide (NCS), are usually carried out in CTC. Although other solvents have been used for this type of reaction it has been shown that the regioselectivity of NBS and NCS reactions can be significantly altered by changing the solvent.[35].

CTC and the chlorofluorocarbons (CFCs) are common solvents for fluorination reactions using molecular fluorine or fluoroxytrifluoromethane (CF_3OF). Fluorine is a highly reactive gas that often breaks carbon chains into smaller units, a side reaction that sometimes becomes troublesome in chlorinations as well. Substitution of other solvents in these reactions would be difficult. Carbon tetrafluoride may be too low boiling in some cases and higher perfluorinated hydrocarbons would probably suffer attack by molecular fluorine. Some such reactions can be carried out using nitrogen as solvent at low temperatures.

Eluent for Chromatography

CTC has found use as an eluent for gas chromatography because it is relatively volatile and is a good solvent. Again these physical features are found in many other common laboratory solvents and therefore, CTC use could cease in the majority of cases for this purpose. In some cases, its use as a eluent may be stipulated for analytical procedures and substitutes will require regulatory approval.

Spectroscopy

Samples for infra-red (ir) spectroscopy analysis can be prepared in various ways. Gaseous samples can be introduced directly into a cell containing ir transparent windows. Liquid samples are often run as thin films between two ir transparent plates, of which sodium chloride and potassium bromide plates are the most common. Spectra of solids may be obtained by grinding the solid in a drop of liquid paraffin (Nujol) and then pressing the sample between two plates as for liquids. Nujol absorbs ir in the C-H region so alternative methods must be used if this region is important. Solid samples may also be ground with potassium bromide and pressed into thin disks and this method often gives the most satisfactory ir spectra for both solids and liquids.

Molecular interactions of interest may change markedly from the solid state or neat liquids to those found in solution, and ir spectra taken in dilute solutions of non polar solvents are normally better resolved. For these reasons, ir spectra are sometimes recorded in a sample cell where the analyte is dissolved in a suitable solvent. Obviously, the solvent must not significantly absorb ir radiation in the region of interest. CTC is one of the best solvents for this purpose because it only absorbs ir radiation in narrow bands and in areas that are usually of little interest. Other solvents which may be used include alcohol free chloroform and carbon disulfide.

CTC is used in certain applications as a transparent spectroscopic medium in ultra-violet spectroscopy, which is usually effective for the identification of substances that have an absorption band in the ultra-violet range, for instance, nitrogen or aromatic compounds.

Trace components which have fluorescence or substances which have an affinity with appropriate fluorescent agents can be identified in low concentrations by fluorescence spectroscopy. CTC is used as a non-fluorescent carrier solvent.

Nuclear magnetic resonance (n.m.r.) spectroscopy is used extensively for the identification of substances which have complex molecular structures. CTC is used as the most appropriate solvent in many cases due to its solvency characteristics and unique chemical structure. In some circumstances deuterochloroform is an effective substitute.

The quantities of CTC used for these purposes are small; usually requiring 1 ml or less for each sample. CTC is very useful for this purpose and for specialist applications in most cases it would be difficult to substitute.

Analysis Standard

Carbon tetrachloride is also used as an analysis standard in various analytical procedures [36]. One such example is as a component of the Karl Fisher reagent, which is used to determine the water content of a variety of substances. In this case a number of alternative reagents and techniques are currently under development.

CTC is used as a calibration standard for the monitoring of atmospheric concentrations of CTC and similarly for the monitoring of CTC concentrations in water. There is obviously little space for alternatives to CTC in these applications.

6.4.3 Agricultural and Veterinary Uses

CTC is known to have been used in two main areas: as an insecticide fumigant, especially in stored grain and cereal products; and as a veterinary antihelmintic agent, especially for the treatment of liver fluke in sheep.

There seems to be no documented evidence of either use currently, although there are suspicions that CTC is still used in certain countries because it is cheap. Amounts are likely to be small and declining.

CTC was used as a bulk grain fumigant in Africa up to 10 years ago. Currently its use would be very limited at the individual farmer level.

CTC is possibly still used as an anti-fluke agent in Nepal and Sudan, but generally there is worldwide distribution of much better drugs that are not expensive.

6.4.4 Chlorine Production

CTC is used in chlorine production to prevent the build up of potentially explosive concentrations of nitrogen trichloride (NCl_3).

The NCl_3 is formed by reaction between chlorine and traces of nitrogen in the original raw material, brine (NaCl), during the electrolytic process which produces chlorine and caustic soda (NaOH).

A number of companies pass the chlorine which contains the trace levels of NCl_3 through CTC which dissolves out the potentially explosive product. The CTC is then destroyed by incineration. Because of the strict guidelines pertaining to the handling of chlorine this process is totally enclosed.

There are a number of alternatives which can be adopted to prevent the build up of NCl_3. These vary depending upon the source of the nitrogen in the brine and include:

a) Removal of nitrogen from the brine prior to chlorine production

- if in the form of ammonia, acidify and strip to remove
- if ferrocyanide-based destroy with chlorine
- removal by raising temperature of brine to >100°C.

b) Destroy NCl_3

- use UV-light reactor to destroy NCl_3.

A number of alternatives exist for the destruction or prevention of formation of NCl_3 in chlorine production that could be adopted over the next few years, although probably not within the current CTC phase out schedule. In many circumstances where the CTC containing residues are incinerated, the use may be considered as non-dispersive.

6.5 Options for Replacement

In some applications, no replacement for CTC will be required because either the application is being phased out, or the CTC is chemically transformed during the process or is completely destroyed or recycled. These applications are described in Section 6.3 above.

No general substitute has been identified for CTC, although progress in certain specific cases has been made. In its application as an inert solvent in chlorination reactions no substitute has yet been identified. It should be possible by application of containment technology to minimize CTC emissions. It should be noted that where CTC is used as a inert reaction solvent for chemical production any change may require time for regulatory approval. With reduced CTC production as a result of CFC phase out, there may be problems in obtaining CTC of sufficient purity for these applications.

6.6 Recovery and Recycling

In the majority of cases CTC used as an inert reaction solvent is recovered in the production process and re-cycled in-house. When recycling is inappropriate, for example, when the CTC becomes unsuitable for continued use, it is available for reclamation or destruction.

Where destruction follows use of CTC in a totally enclosed systems, emissions of CTC to the environment can be considered as insignificant.

6.7 Emission Minimization

It is essential that all emissions of CTC are minimised during manufacture and use. To provide additional guidance to facility operators, a "Code of Good Housekeeping" has been prepared, based on a similar code prepared by the UNEP Destruction Technical Advisory Committee. This code is also intended to provide a framework of practices and measures that should be adopted at facilities undertaking the use of CTC.

Not all measures will be appropriate to all situations and circumstances and as with any Code, nothing specified should be regarded as a barrier to the adoption of better or more effective measures if these can be identified. The suggested Code of Good Housekeeping is described in Appendix 6.

6.8 Developing Country Perspective

Some developing countries have small chlorinated rubber manufacturing facilities. It is believed that at present, one or two other facilities using outdated technologies are being re-installed or are in the planning stages.

The dispersive use of CTC in developing countries is small and is principally for cleaning applications. Alternatives already exist and are widely available as discussed in the UNEP Solvents, Coatings and Adhesives Technical Options Report. In those countries that continue to produce CFCs it is likely that CTC will still be used for this and other applications.

6.9 Summary and Conclusions

World production and consumption of CTC will reduce substantially as manufacture of CFC 11 and CFC 12 is reduced and phased out. Some inadvertent production will continue as a result of other chlorinated processes. Control technology will keep emissions of this material to a minimum.

A number of important chemical processes will continue to use CTC as a feedstock in which the CTC is either destroyed or chemically transformed. These processes will include chemical feedstock for pharmaceutical and agrochemical production, 'catalyst sweetening' and sulphur trioxide stabilisation. Total use in these areas is estimated to be less than 5000 tonnes per annum.

A number of alternatives, such as other chlorinated or inert solvents, have been identified for certain uses of CTC as an inert solvent for chlorination reactions. Alternatives can only be identified on a case by case basis. In principle, by the application of containment technology and the use of thermal oxidation to destroy CTC-containing process residues, CTC emissions can be virtually eliminated from these applications. As a result total usage should reduce rapidly.

In these circumstances, the CTC use as chemical process agents is effectively non-dispersive except for insignificant emissions. A decision will be required by the Parties to define and consider what control measures are appropriate for these applications.

There has currently been little effort in the development of alternatives to CTC for analytical and laboratory applications. Further, many users of CTC are unaware of its role in ozone depletion, contributing to the lack of development of alternatives. A number of national and international laboratory standards specify the use of CTC as a solvent, these will require amendment by the relevant authorities.

At this time the committee supports the concept of a global exemption for laboratory uses of CTC with appropriate controls as described in the March 1994 report of the UNEP Technology and Economic Assessment Panel. A decision will be required by the Parties on whether these analytical and laboratory uses should be controlled and, if so, by what mechanism.

REFERENCES

[3] Grant Thornton Report 1993, Alternative Fluorocarbons Environmental Acceptability Study, August 1993.

[26] Lewis, R. J., Sax's Dangerous Properties of Industrial Materials, Vol. II, 8th Ed., Van Nostraand Reinhold, New York 1992.

[27] Friedlina, R. Kh., Velichko, F. K., *Synthesis*, 145, 1977.

[28] Appel, R., *Angew. Chem. Int. Ed. Engl.*, **14**, 801, 1975.

[29] Isaacs, N.S., Kirkpatrick, D., *Tetrahedron Lett.*, 3869, 1972.

[30] Appel, R., Warning, K., Ziehn, K. D., *Ber Deutsch Chem. Ges.*, **107**, 698, 1974.

[31] Rabinowitz, R., Marcus, R., . *J Am. Chem Soc.*, **84**, 1312, 1962; Chapleur, Y., *J Chem. Soc. Chem. Commun.*, **7**, 449, 1984; Suda, M., Fukushima, A,. *Tetrahedron Lett.*, **22**, 759, 1981; Tanaka, H., Yamashita, S., Yamanoue, M., Torii, S., *J. Org. Chem.*, **54**, 444, 1989.

[32] Barton, D.H. R., Crich, D., Motherwell, W.B., *Tetrahedron Lett.*, **24**, 4979, 1983.

[33] Newman, M. S., Pinkus, A. G., *J. Org Chem.*, **19**, 978, 1954.

[34] Citron, J. D., Lyons, J.E., Sommer, L.H., *J Org Chem.*, **34**, 638, 1969.

[35] Offerman, W. and Vogtle F., *Angew Chem. Int. Ed Engl.*, **19**, 464 1980.

[36] "Annual Book of ASTM standards", American Society for Testing and Materials, 1991

APPENDIX I

TOTAL EQUIVALENT WARMING IMPACT (TEWI) OF SOLVENT ALTERNATIVES

Total Equivalent Warming Impact (TEWI) provides an important tool in the selection procedure for alternative cleaning and drying technologies. However, TEWI must not be the only criterion when selecting the cleaning, drying, or other technology for a manufacturing process. The Alternative Fluorocarbons Environmental Acceptability Study (AFEAS) has provided a methodology to calculate TEWI for wide range of available systems.

The selection of the best technology to displace CFC-113 or 1,1,1-trichloroethane (methyl chloroform) must be specific to the intended applications and will represent a trade-off or balancing of several key parameters: worker safety (toxicity or flammability concerns), investment, operating costs, energy efficiency and reliability. It must also consider a series of environmental issues (discharges to water or landfill, local environmental air quality (smog) and global impact).

This report has evaluated one of the selection parameters, TEWI, for a number of systems. A summary of the key findings follows.

- Solvent losses from the cleaning equipment are potentially lower than assumed in the 1991 study, resulting in lower calculated contributions to TEWI. This reduction in emissions is possible through the adoption of enhanced vapour recovery and improved/novel approaches to materials handling (e.g., freeboard dwell). In some cases, the above technologies can be retrofitted to very modern existing equipment, with results almost comparable to new equipment. However, such equipment will require careful operation and maintenance to sustain low emission rates.

- The no-clean systems used for the manufacture of printed wire assemblies have the potential for the lowest TEWI. For metal cleaning, chlorocarbon-based systems (e.g., perchloroethylene, 1,1,1-trichloroethane) have the potentially lowest TEWI. However, these chlorinated solvent systems may be subject to various national, regional and/or local regulations or emission limits that may severely limit the use of these chemicals for cleaning applications.

- The perfluorocarbon (PFC) system studied has the highest TEWI.

- While they use more energy per unit of work (throughput), aqueous, semi-aqueous and alcohol systems generally have been shown to have a lower TEWI than hydrochlorofluorocarbon (HCFC) and hydrofluorocarbon (HFC)-based systems because emissions from aqueous, semi-aqueous, and alcohol systems do not contribute to global warming.

- In the case of HCFC/HFC/PFC-based systems, the direct effect caused by emission of the chemical, represents from 40 percent to over 90 percent of the calculated contribution to potential global warming.

Future study should assess the effects of variations in equipment and practices on TEWI and estimate implementation time for alternative systems in developing countries.

REFERENCES

Abar Ipsen. 1991 (May 8). Abar Ipsen Industries, Bensalem, P.A. Telefax transmitted to Darrel Staley, Boeing Military Airplanes.

ABLCRS. 1986 (January). The Association of British Laundry, Cleaning, and Rental Services Ltd., Middlesex, England. "Safety in Dry Cleaning Guidelines."

Adhesives Age. 1988. October 1988. p. 49.

Ahmadzai, H. 1989a (May). Principal Executive Officer, National Environmental Protection Board, Sweden. Telefax transmitted to Sudhakar Kesavan, ICF Incorporated, Fairfax, VA.

Ahmadzai, H. 1989b (May). Principal Executive Officer, National Environmental Protection Board, Sweden. Telefax transmitted to Sudhakar Kesavan, ICF Incorporated, Fairfax, VA.

Ahmadzai, H. 1989c (June). Principal Executive Officer, National Environmental Protection Board, Sweden. Telefax transmitted to Sudhakar Kesavan, ICF Incorporated, Fairfax, VA.

Ahmadzai, H. 1989d (July). Principal Executive Officer, National Environmental Protection Board, Sweden. Communication to Sudhakar Kesavan, ICF Incorporated, Fairfax, VA.

Ahmadzai, H. 1991. Comments on the second draft 1991 UNEP Technical Options Report.

Algotsson, K. 1989 (April). SAAB-flyg Division, Linkoping, Sweden. Personal communication to Dr. Ahmadzai, Head of Section, National Environmental Protection Board, Sweden.

American Society for Metals. 1964. Metals Handbook, Volume 2, 8th Edition. pp. 317-325.

Annexe VII to the report of 2nd mtg of participants of Montreal Protocol Ch. 1.2

ANSI/IPC-SC-60. 1987 (October). Post Solder Solvent Cleaning Handbook. Presented to the UNEP Solvents Committee by Dr. Ahmadzai, Head of Section, National Environmental Protection Board, Sweden.

Arvensen, J. 1989. Studsvik Nuclear, S-61182, Nykoping, Sweden.

Asahi Glass. 1989 (February 6). Asahi Glass Company, Ltd., Chemicals General Division, Tokyo, Japan. Press release regarding new substitutes for CFC-113.

Ashland Chemical. 1988. Industrial Chemicals and Solvents Division of the Ashland Chemical Company, Columbus, OH. Solvent Properties Chart.

ASM. 1982. American Society for Metals, Metals Park, OH. Metals Handbook. "Surface Cleaning, Finishing, and Coating." 9th ed., Vol.5.

Attalla, Gary. 1988 (December). Vitronics/Gram Corporation, Newmarket, NH. "Designing Cleaning Equipment for the Terpene Alternative." Surface Mount Technology. pp. 43-45.

Baker, J. 1990. Comments on 1989 UNEP Technical Options Report.

Bakszt. 1988 (November). Report from a visit to alcohol equipment and solder paste manufacturers (in Swedish), Ericsson Research and Development Report SX/MKF 8870.

Balwanz, W.W. 1979. Mattox, Incorporated, Alexandria, VA. "Plasma Cleaning of Surfaces." Published in Surface Contamination: Genesis, Detection, and Control by Mittal, K.L. Volume 1, pp. 255-266.

Barton, Allan F.M. 1983. Handbook of Solubility Parameters and Other Cohesion Parameters. CFC Press: Boca Raton, Florida, USA.

Basu, R.S. 1989 (June 23). Allied-Signal, Buffalo, NY. Transcribed telephone conversation with Thomas R. Hok, ICF Incorporated, Fairfax, VA.

Basu, R.S. and Bonner, J.K. 1989. "Alternatives to CFCs: A New Solvent for the Electronics Industry."

Baxter, B.H. 1989 (May). Chief Materials Scientist, British Aerospace (Dynamics and LTD. U.K.). Telefax transmitted to Sudhakar Kesavan, ICF Incorporated, Fairfax, VA.

Baxter, B.H. 1991. Comments on the second draft 1991 UNEP Technical Options Report.

Bellar, J.M., et. al. 1988 (November). "Substitution of Wax and Grease Cleaners with Biodegradable Solvents Phase I Report." AFESC, Tyndall Air Force Base, FL.

Bentley, D.J. 1983. Update on High Solids and Water-Borne Laminating Adhesives. Package Printing. February 1983. pp. 10-49.

Bernstein, Stan and Green, James. 1981. "Mass Soldering and Aqueous Cleaning Processes Operated in Compliance with Water Pollution Regulations." Electronic Packaging and Production.

Bluestein, C. 1982. pp. 19-22. Radiant Energy Curable Adhesives. Adhesives Age. December 1982.

Boeing. 1991 (August 20). Telefax from Raymond Watkins functional test, Boeing Commercial Airplane Group to Darrel Staley, Boeing Military Airplanes.

Bonner, Kirk. 1991. Comments on the first draft 1991 UNEP Technical Options Report.

Branson. 1988. Branson Ultrasonics Corporation, Danbury, CT. Manufacturer's product literature.

Brazing and Soldering. 1988 (Spring). "Consequences of the Use of CFC Solvents in the Electronics Industry." No. 14. pp. 62-3.

British Aerospace. 1990. Company literature.

Brox, M. 1989a. CFC Elimination Template - NTL Operations (DRAFT). August 1989.

Brox, M. 1989b. Verbal Communication with Sudhakar Kesavan, ICF Incorporated. July 1989.

Bruensbach, Rex. 1987 (October). "Batch Aqueous Cleaning." Printed Circuit Assembly. pp.11-16.

Caci. 1987 (June 22). Electrical Engineer, Raytheon Data Corporation, Waltham, MA. Transcribed telephone conversation with ICF Incorporated, Washington, DC.

Carpenter, C.J. 1989 (April). U.S. Air Force Engineering and Services Center, HQ AFESC/RDVS, Tyndall Air Force Base, FL. Presentation at a UNEP Solvents Committee meeting.

Chao and Hernisch. 1986 (February). Adhesives Age.

Chemical Week. 1987. Adhesives and Sealants: A Booming $4 Billion Business. March 18, 1987. pp. 26-48.

Chem Systems. 1989. The Outlook for Methyl Chloroform Consumption.

Chemtronics, Inc. 1989. Company Literature.

Clark, M. 1991a. Comments on 1989 UNEP Technical Options Report.

Clark, M. 1991b. Comments on the November draft 1991 UNEP Technical Options Report.

Clementson, J. 1988a (January). ICI Solvents Marketing, Runcorn, England. "CFC-113 Conservation and Recovery Practice in Europe." Paper presented at the Substitutes and Alternatives to CFCs and Halons Conference and Trade Fair. Washington, DC.

Clementson, J. 1988b (January). ICI Solvents Marketing, Runcorn, England. "Alternatives for CFC-113 in the Electronics Industry." Paper presented at the Substitutes and Alternatives to CFCs and Halons Conference and Trade Fair. Washington, DC.

Clementson, J. 1988c (January). ICI Solvents Marketing, Runcorn, England. "Reducing Dependence on CFC-113 Solvent in the Electronics Industry." Substitutes and Alternatives to CFCs and Halons Conference and Trade Fair, Washington, DC.

Daikin Industries. 1989. Presentation to UNEP Solvents Committee in Tokyo, Japan.

Damali, K.R., et al. 1975. Environmental Science and Technology, 10, 692.

Danford, Anita L. and Gallagher, Paul A. 1987. Hewlett Packard. "SMD Cleanliness in an Aqueous Cleaning Process." Proceedings at NEPCON East, pp. 245-255.

D'Autilio, D.A. 1983. Solventless Laminating Adhesives. Paper Synthetics Conference.

Dawnkaski, R. 1991. Comments on 1989 UNEP Technical Options Report.

Denpa Shinbun. 1989 (June 8). Summary of article concerning "Ice cleaning apparatus." p. 1.

Dickinson, B.A.; Guth, L.A.; and Wenger, G.M. 1989 (March). "Advances in Cleaning Surface Mount Assemblies." Presented at NEPCON West.

Dow. 1984. Dow Chemical Company. Brochure on Chorethene SM.

DuPont. 1978. DuPont De Nemours and Company, Wilmington, DE. Bulletin #FS-6. Freon Solvent Properties Comparison Chart.

DuPont Electronics. 1989. DuPont Electronics, Wilmington, DE. Technical Brief Development Product TB-DP-El.

Economic Report of the President. 1989 (January). Transmitted to Congress.

Eden News Edition. February 9, 1989.

Ellerhorst, H. Jr. 1982. Industrial Adhesive Markets: A Profile for the 1980s. Adhesives Age. January 1982. pp. 42-48.

Elliott, Donald and Gileta, John. (undated). In-Line High Pressure Solvent Cleaning of Surface Mounted Assemblies. Part 1.

Ellis, B.N. 1986. Cleaning and Contamination of Electronics Components and Assemblies. Electrochemical Publications. Ayre Scotland.

Ellis, B.N. 1987 (Spring). "Aqueous Cleaning of Surface Mounted Assemblies." Brazing and Soldering. No. 12.

Ellis, B.N. 1988a (November 8). Protonique S. A., CH-1032 Romanel-sur-Lausanne, Switzerland. PCIF Course on Cleaning Electronic Assemblies. Oxford.

Ellis, B.N. 1989. Comments on CFC-113 Use in the Electronics Industry. Memo to the U.S. Environmental Protection Agency, Washington, DC.

Ellis, B.N. 1991a. Comments on 1989 UNEP Technical Options Report.

Ellis, B.N. 1991b. Comments on December Draft 1991 UNEP Technical Options Report.

Evanoff, S.P. 1988 (October). Personal communication with Carl Fromm, Jacobs Engineering Group, Pasadena, CA.

Evanoff, S.P. and Weltman, H.J. 1988 (August). "Alternatives to Chlorinated Solvent Vapor Degreasing - Testing, Evaluation, and Process Design." Process Technology '88, Sacramento, CA.

Evanoff, S.P. 1989 (June). Telefax to Sudhakar Kesavan, ICF Incorporated, Fairfax, VA.

Evanoff, S.P. 1994 (August). Comments on 1991 UNEP Solvents, Coatings, and Adhesives Technical Options Report.

Exxon. 1994. Exxon Chemical Company. Safe and Effective Solvents for Drycleaning. Product Literature.

Exxon Chemical Co. Southwest Chemical Co., Solvent Properties Reference Manual.

Felty, J.R. 1986 (February). "SMD vs. PTH Cleaning Requirements: 1975 to 1986." Proceedings of NEPCON West, Anaheim.

Felty, J.R. 1988 (February). "Alternatives for Reducing CFC Cleaning Solvent Dependency." Proceedings of NEPCON West, Anaheim.

Felty, J.R. 1991. Comments on 1989 UNEP Technical Options Report.

Fischer, John. 1991 (August). Comments on the First Draft 1991 UNEP Technical Options Report.

FitzGerald, A.D. 1989a. "Manual of CFC-113 Solvent Management Practices (Draft)" to ICF, April 1989. Transmitted to Sudhakar Kesavan, ICF Incorporated, Fairfax, VA.

FitzGerald, A.D. 1989b. Telefax to ICF regarding activated charcoal systems, costs, and efficiencies. July 1989.

FitzGerald, A.D. 1989c (May). Director, Environmental Affairs, Northern Telecom Limited, Mississauga, Ontario, Canada. Telefax transmitted to Sudhakar Kesavan, ICF Incorporated, Fairfax, VA.

Fries, J.A. 1981. The Growing Uses of Water-Based Adhesives. Paper, Film and Foil Converter. December 1981.

Fries, J.A. 1984. Laminating Adhesives: Present and Future Needs. Part II. Paper, Film and Foil Converter. pp. 60-64.

Frisch, K.C. and Xiao, H.X. 1988. Formulating Polyurethane Adhesives and Sealants. Adhesives Age. September 1988. pp. 41-54.

Fullhart, L., and Mottershead, G.G. 1980. An Overview of the Hot Melt Adhesives Market. Adhesives Age. September 1980. pp. 41-43.

Glas, L.E., M. Ostman, A. Ostman. 1989 (June). "Alternativa Mojligheter Fill 1,1,1-trikloretan i Avfettning/rengoring och Elekronik," Unpublished report to the National Environmental Protection Board, Sweden.

Golden, J.L. and McCain, D.D. 1988 (May). Boeing Aerospace. "Elimination of Vapor Degreasing by Emulsion Cleaners." Presentation to the Aerospace Industry Waste Minimization Symposium, Los Angeles, CA.

Grumman Aircraft. 1990. Company literature.

Guth, Leslie. 1989a (May). "Low Solids Flux Technology for Solder Assembly of Circuit Packs." To be published in Proceedings of Electronics Components Conference, Houston, TX in May 1989.

Guth, Leslie. 1989b (June). "The Selection and Application of Soldering Fluxes to Negate Cleaning Needs." NEPCON East Presentation, June 1989.

Guth, Leslie. 1990 (September). "Applicability of Low Solids Fluxes." Proceedings of U.S.-Singapore Conference Cum Exhibition on CFC Alternatives, Singapore.

Guth, Leslie. 1991. Comments on 1989 UNEP Technical Options Report.

Hayes, Michael. 1988 (December). "Cleaning SMT Assemblies Without Halogenated Solvents." Surface Mount Technology. pp. 37-40.

Hoffman, John. 1988. "Solvent Emission Reduction." IPC-TP-707, Institute for Interconnecting and Packaging Electronics Circuits, Evanston, IL.

Hoffmann, M. 1989a (March). Siemens AG, Geratewerk Erlangen, West Germany. Personal communications to Dr. H. Ahmadzai, Head of Section, National Environmental Protection Board, Sweden.

Hoffmann, M. 1989b. Siemens AG, Geratewerk Erlangen, Federal Republic of Germany. Paper presented at the Conference on CFC Phaseout in the Electronics Industry, Stockholm, 7-8 June, 1989.

HSIA. 1987 (June). Halogenated Solvents Industry Alliance, Washington, DC. White Paper on 1,1,1-Trichloroethane.

HSIA. 1989a (February). Halogenated Solvents Industry Alliance, Washington, DC. White Paper on Perchloroethylene.

HSIA. 1989b (February). Halogenated Solvents Industry Alliance, Washington, DC. White Paper on Methylene Chloride.

HSIA. 1989c (April). Halogenated Solvents Industry Alliance, Washington, DC. White Paper on Trichloroethylene.

Hunt, Don. 1991 (July). Comments on the first draft 1991 UNEP Technical Options Report.

ICF Incorporated. 1987a (October 16). "Regulatory Impact Analysis: Protection of Stratospheric Ozone." Draft of Volume III, Addenda to the Regulatory Impact Analysis Document, Part 7: Solvents, submitted to the Office of Air and Radiation, U.S. Environmental Protection Agency, Washington, DC.

ICF Incorporated. 1987b (October 22). ICF Incorporated, Fairfax Virginia. "Use and Substitutes Analysis of Chlorofluorocarbons in the Electronics Industry." Draft report prepared for the Office of Air and Radiation, U.S. Environmental Protection Agency, Washington, DC.

ICF Incorporated. 1988 (March). "Assessment of Chlorinated Solvent Usage and Control Costs in Metal Cleaning and Electronics Cleaning." Draft Report for U.S. Environmental Protection Agency, Washington DC. Contract No. 02128-318.

ICF Incorporated. 1989a (February 14). "Use and Substitutes Analysis of Methyl Chloroform (1,1,1-trichloroethane)" Draft report prepared for the Global Change Division, Office of Air and Radiation, U.S. Environmental Protection Agency, Washington, DC.

ICF Incorporated. 1989b (October). "Costs of Controlling Methyl Chloroform in the U.S." Draft report prepared for the Global Change Division, Office of Air and Radiation, U.S. Environmental Protection Agency, Washington, D.C.

IPC. 1985. Institute for Interconnecting and Packaging Electronics Circuits. Evanston, IL. "Post Solder Solvent Cleaning Handbook." Working Draft. IPC-5C-60.

IPC. 1986. Institute for Interconnecting and Packaging Electronics Circuits. Evanston, IL. "Post Solder Aqueous Cleaning Handbook."

IPC. 1987. Institute for Interconnecting and Packaging Electronics Circuits. Evanston, IL. "Post Solder Solvent Cleaning Handbook."

Ishii, Yoshiyuki. 1991. Comments on the first draft 1991 UNEP Technical Options Report.

Jancuk, Wilma; Vincent Corsaro; and Chung, Bryan. 1983. "Aqueous Detergent for Removing Rosin Fluxes." Western Electric Engineering (U.S.A.). Vol.27, No.1, pp.63-68.

Joback, K.G. "Replacing 1,1,1-Trichloroethane," Molecular Knowledge Systems.

Joback, K.G. "Material Substitution by Chemical Product Design," Molecular Knowledge Systems.

Johnson, Peter. 1991 (July). Comments on the first draft 1991 UNEP Technical Options Report.

Karash, K., "Opportunities for Replacing Regulated Chemicals: Solvents and the Electronics Industry." 8 March, 1991.

Kato, S., "Dry Etching Technology Using Alternative Gas for CFC-113," Hitachi Ltd., UNEP Solvent Committee Special Seminar, Tokyo, Japan, 5 September 1991.

Kelly, M. 1988 (October 4). Better Engineering Manufacturing, Baltimore, MD. Transcribed telephone conversation with Thomas R. Hok, ICF Incorporated, Fairfax, VA.

Kenyon, W.G. 1989. Personal Communication from Dr. W.G. Kenyon, DuPont, with Mr. Sudhakar Kesavan, ICF Incorporated, Fairfax, VA.

Kerr, Margaret G. 1988 (October 20). "The CFC Challenge: Conservation and Elimination." Speech given at the UNEP Conference, Hague, Netherlands.

Kerr, Margaret G. 1988. "Industry's Position: Another View". EPA Journal

Kimel, F. 1988. Adhesives and Sealants. Chemical Week. March 16, 1988. pp. 28-71.

Kirk-Othmer. 1983. Encyclopedia of Chemical Technology. Published by John Wiley & Sons, New York, NY. p. 380. v. 21.

Kurita, Hiroshi. 1991a. Comments on the September 1991 draft UNEP Technical Options Report.

Kurita, Hiroshi. 1991b. Comments on the December 1991 draft UNEP Technical Options Report.

Lambert, Leo. 1987 (April 17). ICF Incorporated interviews with Leo Lambert at Digital Equipment Corporation, Tewksbury, MA.

Lambert, Leo. 1990. Comments on 1989 UNEP Technical Options Report.

Landrock, A.H. 1985. Adhesives Technology Handbook.

Lea, C. 1988b. A Scientific Guide to Surface Mount Technology. Electrochemical Publications Ltd., Ayr, Scotland.

Lipiec, J. 1982. Adhesives Age. The Three-Pronged Attack on Pressure-Sensitives. March 1982.

Linford, H.B.; Saubestre, E.B. 1950 (December). Cleaning and Preparation of Metals for Electroplating, Plating, and Surface Finishing. pp. 1265-1269.

Maletsky, A. and Villa, J. 1981. Paper, Film and Foil Converter. September 1981. pp. 52-53.

Maletsky, A. and Villa, J. 1984. The Diversification of Hot Melt Adhesives. Paper, Film and Foil Converter. pp. 52-53.

Manino. 1981. Using Waterborne Adhesives to Bond Rubber Assemblies. Adhesives Age. August 1981. pp. 17-19.

Manko, Howard. 1983 (August). "New Packaging Techniques Force and Reexamination of Cleaning Methods." Electronic Packaging and Production. pp. 68-73.

Manko, Howard. 1986. Soldering Handbook for Printed Circuits and Surface Mounting. Van Nostrand, Reinhold Company, Inc., New York, NY.

Markenstein, Howard. 1983 (April 1). "Solder Flux Developments Expand Choices." Electronic Packaging and Production. pp. 39-42.

Matisoff, Bernard S. 1986. Handbook of Electronics Manufacturing Engineering. Van Nostrand, Reinhold Company, New York, NY.

Matsui, Shiegeo. 1991 (July). Comments on the first draft 1991 UNEP Technical Options Report.

Matsumoto, T., "Degreasing and Cleaning of Vacuum Equipment," Ilvac Japan Ltd., UNEP Solvent Committee Special Seminar, Tokyo, Japan, 5 September 1991.

McBryde, W.L. 1985 (June). "Assembly Process and Equipment Requirements Using Water Soluble Flux on Military Programs." Proceedings of NEPCON East, Boston.

McLaughlin Gormley King 1989. Comments received from David Carlson, Manager, Chemical Division & Environmental Affairs, McLaughlin Gormley King Company, on "Costs of Controlling Methyl Chloroform in the U.S.," EPA Review Draft, October 5, 1989, dated November 3, 1989.

Mertens, Jim. 1991a (August). Comments on the first draft 1991 UNEP Technical Options Report.

Midgely 1991. "Worldwide Consumption of Methyl Chloroform" by P. Midgely (draft in preparation).

Ming, K. 1989. Comparison of Freon with Water Cleaning Processes for Disk Drive Parts; Particles on Surfaces II: Detection, Adhesion, Removal. Edited by K. Mittal, Plenum Press, New York, NY.

Mobjork, L. and Olsson, M. 1989. FFV Aerotech, Subcontractor to Swedish Ministry of Defense, Sweden.

Mocella, M.T. 1991 (April). "The CFC-Ozone Issue in Dry Etch Process Development." Solid State Technology, April 1991, pp. 63-64.

Modern Paints and Coatings (MPC) - No author named. 1994a (April). Radiation Curing 1994: A Special Report. Modern Paints and Coatings. April 1994. pp. 14-15.

Modern Paints and Coatings (MPC) - No author named. 1994b (August). UV/EB Curing Takes Hold in North America and Europe. Modern Paints and Coatings. August 1994. pp. 11-13.

Montreal Protocol on Substances that Deplete the Ozone Layer. 1987. Revised 1990 and 1992.

Moreau, M. 1988. UV Curing Cuts Time and Costs For Solenoid Manufacturer. Adhesives Age. April 1988. pp. 18-19.

Morphy, J.S.; Santosusso, T.M.; and Zimmer, D.J. 1987. Polymer Emulsion Blends as Adhesives for Flexible Packaging. Polymers, Laminations, and Coatings Conference.

Mullen, Jerry. 1984. How to Use Surface Mount Technology. Texas Instrument Publishing Center. Dallas, TX.

Nemoto, Y. 1989. Toshiba. Presentation to the UNEP Solvents Committee in Tokyo, Japan.

Niemi, Carol. 1991. Comments on 1989 UNEP Technical Options Report.

Nikkei Sangyo Shinbun. 1989 (June 8). Summary of article concerning "ice cleaning apparatus." p. 11.

Nikon. 1989 (May 24). Japan. Presentation to the UNEP Solvents Committee regarding 2,2,3,3,3-Pentafluoropropanol.

Nilsson, S. 1988 (November 3). Ericsson Telecom AB, Box 193, S-641 22 Katrineholm, Sweden. Letter (in Swedish). Ref. SX/K 811 to National Environmental Protection Board, Sweden.

Nordin, N.O. 1988 (November). Action Plan for a Freon Free Lubrication of Contacts (in Swedish). Ericsson document, SX/KV 866.

Northern Telecom. 1989. Northern Telecom Limited, Mississauga, Ontario, Canada. CFC Program.

NTP. 1984. Annual Plan for Fiscal Year 1984. DHHS. Public Health Service, Research Triangle Park, NC. NTP 84-023.

NUCON International, 1991. Product Literature.

Oakite Products, Incorporated. 1988. "Metal Cleaning Fundamentals, Materials, and Methods." Manufacturer's product literature.

O'Driscoll, M. 1988. Minerals in Adhesives and Sealants: Solving a Sticky Problem. Industrial Minerals. February 1988. pp. 32-51.

Ortho 1989. Comments received from William L. Chase, Jr., Manager, Registration and Regulatory Affairs, Orhto Chevron Chemical Company, on "Costs of Controlling Methyl Chloroform in the U.S.," EPA Review Draft, October 5, 1989, dated November 1, 1989.

Owens, J. 1990 (Sept.). 3M Company. "Alternative Solvent for Fluorocarbon Lubricant Deposition," presented at Diskcon '90, San Jose, CA, September 1990.

Patterson, K. and Hunt, D. 1989. Newark Air Force Base, Aerospace Guidance and Meteorology Center, Newark, OH. "The Cyl-Sonic Cleaner: Aqueous Ultrasonic Cleaning Using Biodegradable Detergents."

Pawling, J.A. 1987. Surface Mounted Assemblies. Electrochemical Publications, Ayr, Scotland.

PEI. 1983. Pedco-Environmental Inc., Consulting Associates, Cincinnati, OH. "Industrial Process Profiles for Environmental Use." Chapter 30, "The Electronic Component Manufacturing Industry." EPA-600-283-033. U.S. Environmental Protection Agency, Washington, DC.

Phasex Corporation, 360 Merrimack St., Lawrence, MA 01843.

Prane, J.H. 1980. Reactive Adhesives. Adhesives Age. August 1980. pp. 35-37.

Racquet, D. 1988 (September 22). Phillips Manufacturing Company, Chicago, IL. Transcribed telephone conversation with Thomas R. Hok, ICF Incorporated, Fairfax, VA.

Radian. 1986a. Radian Corporation, Durham, NC. "Evaluation of Potential Ozone Depleting Substance Emissions and Controls." Prepared for the Office of Air and Radiation, U.S. Environmental Protection Agency, Washington, DC.

Radian Corporation. 1987 (March). Responses to Section 114 Questionnaires. Survey conducted for Chemical and Petroleum Products Division, Office of Air Quality, Planning, and Standards, U.S. Environmental Protection Agency, Washington, DC.

Randall, F. 1988a (November 7). Ramco Equipment Corporation, Hillside, NJ. Transcribed telephone conversation with Thomas Hok, ICF Incorporated, Fairfax, VA.

Randall, F. 1988b (October 25). Ramco Equipment Corporation, Hillside, NJ. Transcribed telephone conversation with Thomas Hok, ICF Incorporated, Fairfax, VA.

Report EUR 9510 EN. 1984. "Code of Practice for the Design, Construction, and Operation of CFC-113 Degreasers." Published by the Commission of the European Communities, Directorate-General Information and Market Information, Luxembourg.

Rodgers, J.E. 1989 (June 6). Letter to Stephen O. Andersen, U.S. Environmental Protection Agency, Washington, DC, from J.E. Rodgers, Allied-Signal Incorporated, Engineered Solvent Systems, Morristown, NJ.

Russo, John and Fischer, Martin. 1989 (March 8). Separation Technologists Inc. "Closed-Loop Water Recycling for PWB Aqueous Cleaners." Presented at NEPCON West.

Schaefer, J. and Scott, S. 1991 (January). "Single-Point Diamond Machining of Optical Components," Texas Instruments Technical Journal, Volume 8, Number 1. March-April 1991, pp. 105-114.

Schneider, Alvin. 1987 (June 9-11). "Wave Soldering Flux Development and Trends." Paper given at NEPCON East. Boston, MA.

SEHO. 1988. Seitz & Hohnerlein, Kreuzwertheim, West Germany. General system description and environmental considerations for the Nitrogenius 1 inert gas wave soldering machine.

Seidinger, K. 1989 (March). "Vapour Phase Soldering and the Ozone Depletion Issue." Paper presented at the Joint Societies Technical Conference, Internepcon, Birmingham.

Skeist, Inc. 1987. Adhesives, V: A Multiple Client Study. October 1987.

SNV 1990a. Swedish Environmental Protection Agency, Solna, Sweden. "Technical review of the chemical use of 1,1,1-trichloroethane and carbon tetrachloride, as well as the options for replacing and phasing out the substances.

SNV 1990b. Swedish Environmental Protection Agency, Solna, Sweden. "Technical review of the chemical use of 1,1,1-trichloroethane subarea release agents.

Soble, Richard. 1979 (October). Insulation/Circuits. "Solvent Cleaning of Printed Wiring Assemblies."

SOLTEC. 1988. Preliminary Engineering Data Sheet, Inert Gas Soldering Machine Model 6567, GS 193, Holland

Sprayon 1989. Comments received from Douglas Raymond, Regulatory Affairs, Sprayon Products, Aerosol Specialties, on "Costs of Controlling Methyl Chloroform in the U.S.," EPA Review Draft, October 5, 1989, dated October 31, 1989.

Spring, S. 1974. Industrial Cleaning. Prism Press. pp. 24-26.

Stahl, Bosse. 1989 (April 12). Svenska Krets-Teknik AB, Lumavagen 6 Hus 1C, S-104 80, Stockholm. Personal communication to Dr. H. Ahmadzai, National Environmental Protection Board, Sweden.

Staley, D.A. 1991 (April). Comments by Darrel Staley, Boeing Military Airplanes, on the 1989 UNEP Technical Options Report.

Staley, D.A. 1991 (July). Comments by Darrel Staley, Boeing Military Airplanes, on the 1991 First Draft UNEP Technical Options Report.

Staley, D.A. 1991 (September). Comments by Darrel Staley, Boeing Military Airplanes, on the 1991 Second Draft UNEP Technical Options Report.

Standards Association of Australia. 1987. Australian Standard 1957-1987. "Care, Labelling of Clothing, Household Textiles, Furnishings, Upholstered Furniture, Bedding, Piece Goods and Yarns."

Statch, S. 1979 (November-December). "Water Soluble Fluxes: Can the Military Use Them?" Texas Instruments EG Engineering Journal.

Statch, S. 1980 (May-June). "Water Soluble Fluxes: Phase II Testing." Texas Intruments EG Engineering Journal.

Stemniski. 1991a. Comments on first draft of 1991 UNEP Technical Options Report.

Streckfuss. 1989. Company Literature.

Suciu, Dan. 1989 (February 23). EG&G Incorporated. Transcribed telephone conversation with Peter Weisberg, ICF Incorporated, Fairfax, VA.

Svensson, J. 1989a (June 7-8). "A Strategy to Eliminate CFCs as a Cleaning Agent for PBAs." Paper presented at the Conference on CFC Phase-Out in the Electronic Industry, Stockholm, Sweden.

Svensson, J. 1989b (May 30). Peer review communication to Dr. Stephen O. Andersen, Chief of Technology and Economics Branch, U.S. Environmental Protection Agency.

Taylor, J. 1988 (November 7). Bowden Industries Incorporated, Huntsville, AL. Transcribed telephone conversation with Thomas R. Hok, ICF Incorporated, Washington, DC.

Tisch. 1991. C mments on the first draft 1991 UNEP Technical Options Report.

Toubin, A. 1989. "Low Solids Content Fluxes." Circuit World. Volume 15, No. 2, pp. 17-18.

Umeki, Hiroki. 1989 (April 18). DuPont-Mitsui, Japan. "Water Displacement/Drying with CFCs." Communication submitted to the United Nations Environment Program Solvents Committee.

United Nations Environment Programme (UNEP). 1989 (June). Technical Progress on Protecting the Ozone Layer: Electronics, Degreasing and Dry Cleaning Solvents Technical Options Report.

UNEP. 1991 (December). Solvents, Coatings, and Adhesives Technical Options Report.

UNEP. 1992. Protecting the Ozone Layer: Volume 2 - Solvents, Coatings, and Adhesives. UNEP Industry and Environment Programme Activity Centre (IE/PAC).

UNEP. 1994a. Technologies for Protecting the Ozone Layer: Catalogue - Aerosols, Sterilants, Miscellaneous Uses, and Carbon Tetrachloride. UNEP Industry and Environment Programme Activity Centre (IE/PAC).

UNEP. 1994b. Technologies for Protecting the Ozone Layer: Catalogue - Specialized Solvent Uses. UNEP Industry and Environment Programme Activity Centre (IE/PAC).

Unique Industries. 1988. Unique Industries, Sun Valley, CA. Manufacturer's literature.

U.S. Department of Commerce. 1987. Exchange rates from Statistical Abstracts, U.S. Government Printing Office, Washington, DC. p. 839.

U.S. Environmental Protection Agency (EPA). 1989a (March). U.S. Environmental Protection Agency. Health Effects Assessment Summary Tables. Prepared by the Office of Health and Environmental Assessment. Environmental Assessment and Criteria Office, Cincinnati, OH, for the Office of Solid Waste and Emergency Response, Office of Emergency and Remedial Response, Washington, DC.

U.S. EPA. 1989b (May 1). U.S. Environmental Protection Agency. Integrated Risk Information System (IRIS). Environmental Criteria and Assessment Office, Cincinnati, OH. Revised May 1, 1989.

U.S. EPA. 1989c (June). Communication from James Hemby, Global Change Division of the Office of Air and Radiation, U.S. Environmental Protection Agency, Washington, DC, to the UNEP Solvents Review Committee.

U.S. EPA. 1989d (June). Integrated Risk Information System (IRIS). Environmental Criteria and Assessment Office, Cincinnati, Ohio. Revised June 1, 1989

U.S. EPA. 1991a (June). Alternatives for CFC-113 and Methyl Chloroform in Metal Cleaning. EPA/400/1-91-019.

U.S. EPA. 1991b (June). Aqueous and Semi-Aqueous Alternatives for CFC-113 and Methyl Chloroform Cleaning of Printed Circuit Board Assemblies. EPA/400/1-91/016.

U.S. EPA. 1991c (June). Conservation and Recycling Practices for CFC-113 and Methyl Chloroform. EPA/400/1-91/017.

U.S. EPA. 1991d (June). Eliminating CFC-113 and Methyl Chloroform in Precision Cleaning Operations. EPA/400/1-91/018.

U.S. EPA. 1993 (September). Multiprocess Wet Cleaning: Cost and Performance Comparison of Conventional Dry Cleaning and an Alternative Process. Office of Pollution Prevention and Toxics. EPA 744-R-93-004.

U.S. Patent # 4,821,948 Ch. 2.3.5.1

Van Zant, Peter. 1985. "Microchip Fabrication." Semiconductor Services, San Jose, CA.

Wallace, Leonard R. 1988. "Solvent Recovery Systems." IPC-TP-689, Institute for Interconnecting and Packaging Electronics Circuits, Evanston, IL.

Wang, Alan. 1988 (March 17). LONCO, PO Box 806, Bensenville, IL 60106, U.S.A. Paper presented at Kemiska AB Condor, Lodseminarium, Norrkoping, Sweden.

Wargotz, W.B., Guth, L.A., and Stroud, C.V. 1987 (June 2-5). "Quantification of Cleanliness Beneath Surface Mounted Discretes Assembled by Wave Soldering." Printed Circuit World Convention IV. Tokyo, Japan. WCIV-72.

Weemes, G.C. 1990. ICI PLC, "Design of equipment for use with HCFC cleaning fluids." Presented at 1990 International Conference on CFC and Halon Alternatives, Baltimore, U.S.A.

Weltman, H.J.; Evanoff, S.P. 1991 (May). Replacement of Halogenated Solvent With Aqueous Immersion Cleaners, 46th Annual Purdue Industrial Waste Conference.

Weltman, H.J.; Evanoff, S.P.; and Singer, K. 1988 (May 26). General Dynamics, Fort Worth Division. "Evaluation of Water-Based, Terpene, and Freon Degreasers." Report to Aerospace Industry Waste Minimization Symposium, Los Angeles, CA.

Wenger, George and Munie, Gregory. 1988 (November). "Defluxing Using Terpene Hydrocarbon Solvents." IPC Technical Review, Institute for Interconnecting and Packaging Electronics Circuits, Evanston, IL. pp. 17-23.

Wikoff, P. 1989 (May). Personal communication to Dr. H. Ahmadzai, Head of Section, National Environmental Protection Board, Sweden.

Wolf, Katy; Phillips, Quintin; and Andersen, June. 1988 (November 10). UCLA National Science Foundation. Engineering Research Center for Hazardous Substances Control. Proceedings of Workshop on Replacing CFC-113 in Critical Mechanical Cleaning Applications.

Wood, J.S. 1984. Converter's Experiences with High Solids/Low Solvent Polyester Urethane Laminating Adhesives. Polymers, Laminations, and Coatings Conference 1984.

Wood, W.G. et. al.; American Society for Metals. Metals Handbook, Volume 5, 9th Edition. pp. 20-21.

Yamabe, M. 1991 (June). Comments on first draft 1991 UNEP Technical Options Report.

Yamabe, M. and K. Kitamura. "HCFC-225," Asahi Glass Co., Ltd., UNEP Solvent Committee Special Seminar, Tokyo, Japan, 5 September 1991.

Yoshida, Y., "Dry Etching Technology Using Alternative Gases for Tetrachlorocarbon," Toshiba Corporation, UNEP Solvent Committee Special Seminar, Tokyo, Japan, 5 September 1991.